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JOURNAL

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THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Spectroscopic Examination of the Constituents of the Atmosphere. By J. Janssen (*Compt. rend.*, **101**, 649—651).—At the Meudon Observatory, four absorption-tubes, one of which is 60 metres long, have been set up, and the absorption-spectra of hydrogen, air, and oxygen have been examined, sometimes under high pressures. In the case of hydrogen, an enormous stratum of gas must be employed before any absorption-spectrum can be observed. When oxygen is examined in the 60-metre tube under gradually increasing pressure, successive groups of lines appear. The first are the lines and bands in the red, which Egoroff regards as identical with the lines A and B in the solar spectrum, but if the pressure is raised beyond 27 atmos., and the intensity of the light employed is increased, evidences of absorption are obtained between A and B, and between B and C, but still higher pressures are necessary before the existence of absorption-bands in these positions can be definitely established. At very high pressures, three other bands become visible, one in the red near α, one in the greenish-yellow near D, and one in the blue. No similar bands are known in the solar spectrum. C. H. B.

Optical Properties of Malic and Tartaric Acids. By L. Bell (*Amer. Chem. J.*, **7**, 120—128).—Both tartaric and malic acids show an increase of optical activity with a rise in temperature, or with a decrease of concentration, and in the case of lævo-malic and dextro-tartaric acids, the sign of polarisation is reversed if solutions sufficiently strong and cold are examined. From thermic observations it seems that this change of rotary power cannot be accounted for either by the supposition of changes of configuration of the molecule, or of the formation of hydrates, or of the formation of crystal molecules. It is, however, thought that the change is due to the formation of polymerides, which are gradually decomposed by dilution or

application of heat; in dilute solutions, the changes effected by variation are but slight when compared with those in strong solutions, where one must expect the polymeride to exist in comparatively large proportion. A further proof of the formation of polymerides is the fact that the solutions show abnormal rotary dispersion—a phenomenon not possible with the solution of a single substance—and this may be gradually made normal by dilution or by heating.

Tartaric and malic acids both exist in more forms than can be accounted for on any existing theory; this may possibly be explained by the observation that two molecules of a substance containing an asymmetrical carbon-atom may be symmetrically united in four different ways. H. B.

Sensitiveness to Light of Selenium and Sulphur Cells. By S. Bidwell (*Chem. News*, **52**, 191—193).—With regard to the action of light in diminishing the electrical resistance of selenium, and producing in it a photo-electric current, Adams and Day have observed that in such cases the structure of the selenium is so modified that it behaves apparently like an electrolyte, and hence conclude that selenium, under those conditions, conducts electrolytically.

In the present paper, the author attributes these phenomena to actual electrolysis, and bases this assertion on the following facts.

It is known that in making selenium "cells," the longer they are "annealed" (that is, heated in contact with the metallic electrodes) the more sensitive the selenium becomes to the action of light. Again, a very sensitive selenium "cell" has been constructed by Fritts, in the following manner:—A film of selenium is melted on a plate of metal with which it can combine, and ultimately the other surface is coated with a transparent conductor. Moreover, a piece of selenium contained in a good "cell" with copper electrodes indicated a specific resistance = 0·9 megohm, whilst the resistance of a similar piece of selenium annealed in a glass mould out of contact with metal = 2500 megohms. The author infers that a selenide is formed during the heating with the metal, and that the sensitiveness is due to the presence of the selenide and its electrolysis by the current. To complete the chain of experimental evidence, sulphur, which has hitherto resisted numerous attempts to develop in it the sensitiveness to light so characteristic of selenium, was mixed with silver sulphide, and incorporated in a "cell" with silver electrodes; it then exhibited remarkable sensitiveness to light, and its resistance was greatly reduced by it. Numerous experiments are described proving this effect to be due to the direct action of radiation, and not simply to a rise in the temperature, by which this sulphur "cell" is affected in a similar manner. Electrolytically considered, the action in the sulphur "cell" containing silver sulphide and silver electrodes is this: when the current passes, silver is deposited upon the cathode and sulphur upon the anode, but any sulphur deposited on the anode would stop the current, an occurrence which is prevented by the silver combining with the sulphur, hence the quantity of electricity passing is regulated by the quantity of sulphur disposed of in this manner. By replacing one of the silver electrodes by a metal which does not

combine so readily with sulphur, iron for instance, then on the above hypothesis, when iron is the anode the resistance ought to be greater than when silver is the anode, and such is the case in actual experiment, the resistance being 30 times greater in the former than it is in the latter case. Other experiments show that light assists the direct combination of silver and sulphur, and it is inferred that "the electrolysis of silver sulphide may be assisted by light, and its electrolytic resistance at the same time diminished."

In a few experiments made with sulphur "cells" containing copper and copper sulphide, there was no indication of sensitiveness to light.

With regard to the effect of temperature on selenium "cells," the author has observed that whether exposed to light or not, selenium "cells" have a temperature of maximum resistance, which is generally a few degrees higher than the average temperature of the air. D. A. L.

Dry Electric Batteries. By W. v. Beetz (*Ann. Phys. Chem.* [2], **26**, 13—26).—This paper contains a series of determinations of the electromotive force of certain dry forms of Daniell's battery, especially of those consisting of **U**-tubes containing in the one limb copper sulphate solution, in the other zinc sulphate solution, both being worked up into a paste by plaster of Paris, and then allowed to set in the tubes. Their use as an unit in electric measurements was examined; it was found that in some cases the difference of potential remained constant, whilst in others it decreased very rapidly. Such batteries cannot be used in electro-therapeutics. V. H. V.

New Forms of Thermopiles. By H. Kayser (*Ann. Phys. Chem.* [2], **26**, 9—13).—In this paper, measurements are given of the electromotive forces and resistances of various forms of thermopiles, the source of heat being a gas flame burning a known number of litres of gas per hour. The electromotive force of a Noë-Rebiceck's thermoelectric pile of 20 elements was found to be constant for an indefinite length of time, provided that the external conditions, namely, gas pressure and temperature of the air, were unaltered; its electromotive force also exceeded that of a Bunsen's element. The internal resistance increased to a maximum, with a consumption of gas from 0—60 litres per hour, and from that point to 110 litres per hour it diminished; the maximum resistance of a pile of 25 elements was 0·868 ohm. The relative advantages of a thermopile over a Bunsen's element in cases of small external resistance are also discussed. V. H. V.

Electrical Conductivity of Air under Reduced Pressure. By T. Homén (*Ann. Phys. Chem.* [2], **26**, 55—81).—Experiments on the relation of the conductivity of air to the pressure, have led to the opposed conclusions that an absolute vacuum is a perfect non-conductor, and a good conductor of electricity. In this paper, an elaborate series of experiments on the conductivity of air in discharge tubes under various degrees of pressure are described. The results show that the phenomena of conductivity of air under reduced

pressure are of two kinds, the one, the particular resistance of the air, which is proportional to the distance between the electrodes, the other the actual resistance of the electrodes themselves. The former is independent of the diameter of the air column, and its increase is nearly proportional to the pressure, whilst the latter increases very quickly with decrease of pressure, and under low pressures reaches a point at which the resistance is such that electricity, even at the highest difference of potential, cannot overcome it. These results are not in accordance with the view that a vacuum is a good conductor of electricity. V. H. V.

Electrical Conductivity of Alcohol. By E. PFEIFFER (*Ann. Phys. Chem.* [2], **26**, 31—44).—In this paper a description is given of determinations of the conductivity of absolute alcohol, and the variations produced by change of condition. The lowest value for recently distilled alcohol was $0{\cdot}1261 \times 10^{-10}$ ohms in terms of mercury as the unit. The relative conductivity is increased by the presence of traces of impurities, but decreased to a considerable extent by the absorption of air; it decreases, as that of metals, with rise of temperature, until a point is reached at which the influence of temperature is *nil*. The author proposes to call this point "the point of indifference." Comparing the temperature coefficient, or the ratio of decrease of conductivity, with rise of temperature $= \frac{At}{\lambda^0}$ of alcohol with that of the metals, it is found that the former is to the latter in the ratio 0·0087 to 0·0037. V. H. V.

Electrical Properties of Salt Solutions. By J. MOSER (*Monatsh. Chem.*, **6**, 634—638).—The author has previously investigated the electromotive force of cells in which the total amount of purely chemical reaction is reduced to a minimum, the current being conditioned by the minor molecular attractions of a salt with the water in which it is dissolved; such, for example, is the combination | Zn | dilute $ZnSO_4$ | concentrated $ZnSO_4$ | Zn. From these experiments Helmholtz determined the relation between the E.M.F., the vapour-tension of the salt solution, and the *transference-values* of the ions (compare Faraday lecture, Trans., 1881, 299), so that if two of these values were known the third could be calculated. By the experimental elimination of the third factor, the relation could be determined between the E.M.F., conditioned by difference of concentration and the vapour-tension. Then, if the theories of Helmholtz are compatible in the two cases stated above, the *transference-value* should be the quotient of the E.M.F.'s, with and without a possible transference of the ions.

In the paper this point is examined and found to be in accordance with the theory.

There is also mentioned a case of electro-neutrality of a combination Zn | $ZnCl_2$ | $ZnSO_4$ | Zn, in which the solutions were of such a degree of concentration that the addition of water to either of them produced a current with concomitant transference of the ions.

Attention is also drawn to the fact that the E.M.F., produced by

differences of concentration, does not correspond with the heat changes on dilution. V. H. V.

Incandescence by Ultra-red Rays. By E. Lommel (*Ann. Phys. Chem.* [2], **26**, 157—158).—After alluding to the experiments of Tyndall on the incandescence of platinum by the impact of the ultra-red rays transmitted through a solution of iodine in carbon bisulphide, the author shows that the effects of these rays can be rendered visible by means of the so-called luminous paints, inasmuch as these rays are emitted as a greenish-blue fluorescence. A solution of nigrosin in chloroform or alcohol is proposed as a substitute for iodine in carbon bisulphide as a perfectly opaque but diathermic medium.

V. H. V.

So-called Specific Remission. By W. Ramsay and S. Young (*Ber.*, **18**, 2855—2858).—The authors, after alluding to their various papers on the relation between the pressure and boiling points of liquids (compare Abstr., 1885, 629, Trans., 1885, 640—657) point out the improbability of the relation designated by Kahlbaum "specific remission" (Abstr., 1884, 141, 900), and the sources of error in his method of investigation. The authors' results for the vapour-tensions of ethyl alcohol are in accordance with those of Regnault, although the former were obtained by the dynamical, the latter by the statical method, but those of Kahlbaum are widely divergent from both, and are presumably worthless.

In the equation $\frac{L}{s_1 - s_2} = \frac{dp}{dt}\frac{t}{T}$ (in which L is the latent heat of the vapour, s_1 its volume, s_2 the volume of the liquid, $\frac{dp}{dt}$ the increase of pressure for each degree temperature, t the absolute temperature, and T the heat equivalent of the work), the authors propose to show that the values for $\frac{L}{s_1 - s_2}$ are approximately constant for several liquids, and further, that the ratio $\frac{dp}{dt}\frac{t}{T}$ for two substances A and B at pressure p_1 is equal to that for the same substances at different pressure p_2: that is—

$$\frac{dp}{dt}\frac{t}{T} \text{ for A at } p_1 = \frac{dp}{dt}\frac{t}{T} \text{ for A at } p_2.$$

$$\frac{dp}{dt}\frac{t}{T} \text{ for B at } p_1 = \frac{dp}{dt}\frac{t}{T} \text{ for B at } p_2.$$

or expressed in terms of absolute temperature, $\frac{T_A}{T_B}$ at $p_1 = \frac{T_A}{T_B}$ at p_2.

A list of substances is given for which this relation is valid.

V. H. V.

Modification of Bunsen's Ice Calorimeter. By A. Blümcke (*Ann. Phys. Chem.* [2], **26**, 159—160).—Two forms of Bunsen's ice calorimeter are used; in the one the heat change is measured by the change of position of a mercury thread along a graduated scale, whilst

in the other the instrument is made into an inverted weight thermometer. Both these methods have relative advantages and disadvantages; the latter is more exact, but requires a longer time, whilst the former requires an inordinately long scale. In this paper an instrument is described, by which determinations by both methods can be conducted simultaneously. The experimental tube is closed with a caoutchouc plug, through which pass two pieces of quill tubing, each bent at right angles and provided with stop-cocks, the limb of the one being graduated, the limb of the other being bent again at right angles, and dipping under the surface of a weighed quantity of mercury. Then by opening or closing the stop-cocks determinations are made both by the scale and the inverted weight-thermometer methods. V. H. V.

Phenols. By BERTHELOT (*Compt. rend.*, **101**, 687—690).—*Orthocresol.*—Heat of solution at 11·4° = − 2·08 cal.; heat of neutralisation by soda, first equivalent + 7·79 cal., second half-equivalent + 0·4 cal. = + 8·19 cal.

Paracresol.—Heat of solution at 11·4° = − 2·13 cal.; heat of neutralisation by soda, first equivalent + 7·64 cal., second half-equivalent + 0·43 = + 8·27 cal.

The values obtained are very similar in the case of each isomeride, and they agree closely with those obtained with phenol.

Thymol.—The specimen employed was obtained from oil of thyme, and had been crystallised for thirty years. When dissolved in sodium hydroxide solution, the heat developed is + 5·73 cal., a number very similar to that obtained with solid phenol and the solid cresols under the same conditions. It follows, therefore, that the heats of solution and neutralisation of thymol are practically the same as those of its homologues. Recently fused or precipitated specimens of thymol give different and non-concordant results, because thymol, like chloral hydrate, parts very slowly with its heat of fusion.

α-Naphthol.—Solution in one equivalent of sodium hydroxide solution develops + 2·84 cal., and the addition of a second equivalent of alkali develops + 0·2 cal., giving for the algebraic sum of the heats of solution and neutralisation the value + 3·04 cal. The corresponding values for *β-naphthol* are + 2·19 cal. and + 0·00 cal. = + 2·19 cal.

Quinhydrone (green quinone), $C_6H_4O_2{\cdot}C_6H_4(OH)_2$.—Heat of solution of quinone at 13° = − 3·77 cal., Werner having previously found − 4·23 cal. The mean value is − 4·00 cal. Heat of solution of quinol at 13° = 4·155 cal. Concentrated solutions of the two compounds were mixed, the heat developed was measured, and the amount of quinhydrone which separated was determined. From these data the following values were calculated:—

$C_6H_4O_2$ diss.	+	$C_6H_4(OH)_2$ diss.	= $C_{12}H_{10}O_4$ diss.	+	0·50
$C_6H_4O_2$,,	+	$C_6H_4(OH)_2$,,	= $C_{12}H_{10}O_4$ cryst.	+	17·2
$C_6H_4O_2$ cryst.	+	$C_6H_4(OH)_2$ cryst.	= $C_{12}H_{10}O_4$,,	+	9·0

One part of quinhydrone dissolves in 300 parts of water at 14°.

No thermal disturbance is produced by the addition of an alkali to anthraquinone, phenanthraquinone, phlorone, and similar compounds,

so that in this respect these compounds differ from the true quinones. They are more probably analogous to acetone, allylene oxide, and similar oxy-derivatives of hydrocarbons.

Alizarin when dissolved in one equivalent of sodium hydroxide solution develops + 5·15 cal; the addition of a second equivalent of alkali develops + 0·64 cal., whilst a third equivalent produces no thermal disturbance. It follows that in very dilute solutions alizarin shows only one phenolic function towards alkalis. In this respect it resembles catechol, pyrogallol, and similar compounds of the ortho-series, and hence it would follow that alizarin also belongs to the same series. C. H. B.

Isomerism in the Benzene Series: Phenols of Complex Function. By Berthelot (*Compt. rend.*, **101**, 651—656).—*Para-methoxybenzoic Acid* (anisic acid), $MeO{\cdot}C_6H_4{\cdot}COOH$.—Heat of solution in an equivalent quantity of sodium hydroxide solution = + 5·125 cal.; hence, assuming the heat of neutralisation to be the same as that of parahydroxybenzoic acid, + 13·0 cal., the heat of solution in water is − 7·9 cal. The addition of a second equivalent of alkali causes no sensible further development of heat; hence anisic acid has no phenolic function. This agrees with the commonly accepted constitution of this acid.

Methyl Salicylate, $HO{\cdot}C_6H_4{\cdot}COOMe$.—Heat of solution in one equivalent of alkali + 4·0 cal., in a second equivalent + 0·20 cal. The first value will differ but little from the heat of neutralisation in an aqueous solution, since the solution of one liquid in another is never accompanied by any considerable absorption of heat. The heat of neutralisation of this ethereal salt is therefore comparable with that of a phenol of weak function.

Phenylglycollic Acid (mandelic acid), $HO{\cdot}CHPh{\cdot}COOH$.—Heat of solution at 18° = − 3·09 cal. The addition of half an equivalent of alkali develops + 6·74 cal., a second half-equivalent + 6·88 cal., and a third half-equivalent + 0·24 cal. It is therefore a monobasic acid without any phenolic function.

Vanillin, $OH{\cdot}C_6H_3(OMe){\cdot}CHO$ [4 : 3 : 1].—Heat of solution at 13·7° = − 5·20 cal. The first equivalent of alkali develops + 9·26 cal., a second equivalent produces no thermal disturbance. Methylprotocatechuic aldehyde therefore behaves as a monhydric phenol.

Vanillic Acid, $OH{\cdot}C_6H_3(OMe){\cdot}COOH$ [4 : 3 : 1].—Heat of solution at 13·9° = − 5·16. The first equivalent of alkali develops + 12·64 cal., the second + 9·74 cal., and the third + 1·37 cal. This acid, therefore, behaves as a monobasic acid and a monhydric phenol, as the ordinary formula indicates.

Similar experiments show that piperonal (methyleneprotocatechuic aldehyde), piperonylic acid, piperic acid, veratric acid, anisaldehyde, anisyl alcohol, anisoïl, anethoïl, and salicin have no phenolic function.

Eugenol, on the other hand, behaves as a monhydric phenol. The first equivalent of soda develops + 5·77 cal., the second + 0·86 cal., and the third produces no thermal disturbance.

Toluneparasulphonic acid and sodium benzenesulphonate have no phenolic function.

In all these cases, there is complete agreement between the thermochemical data and the generally accepted constitution of the compounds as deduced from their chemical behaviour. C. H. B.

Acids of the Benzene Series. By BERTHELOT (*Compt. rend.*, **101**, 685—686).—*Mellitic Acid*, $C_6(COOH)_6$.—Heat of solution = + 3·672 cal. at 20·4°; it is therefore a positive quantity, and differs in this respect from the heats of solution of the majority of highly oxidised carbon acids. The heat of neutralisation by successive equivalents of sodium oxide is as follows:—

First equivalent ($\frac{1}{2}Na_2O$) develops				+ 14·80 cal.	
Second	,,	,,	,,	+ 14·70 ,,	= + 44·30.
Third	,,	,,	,,	+ 14·80 ,,	
Fourth	,,	,,	,,	+ 13·60 ,,	
Fifth	,,	,,	,,	+ 12·90 ,,	= + 39·13.
Sixth	,,	,,	,,	+ 12·63 ,,	

The mean value is + 13·90 × 6 cal., which is almost exactly the same as that of benzoic and phthalic acids. The last three equivalents of alkali develop somewhat less heat than the first three, and in this respect also mellitic acid is analogous to phthalic acid.

Meconic Acid, $C_7H_4O_7 + 3H_2O$.—Heat of neutralisation at 12·7° = − 9·10 cal. The quantities of heat developed by the addition of the first, second, third, and fourth equivalents of alkali are respectively + 14·4 cal., + 13·6 cal., + 8·7 cal., + 0·7 cal., and from these results, which are analogous to those obtained by Louguinine with phosphoric acid, it follows that meconic acid is really bibasic, with an accessory function which is either analogous to or identical with the phenolic function.

Acrylacetic Acid (tetric acid), $C_5H_6O_3$.—Heat of solution at 12·7° = − 3·9 cal., heat of neutralisation + 12·5 cal. A second equivalent of alkali produces no sensible thermal disturbance, and therefore acrylacetic acid is a monobasic acid of simple function.

It is worthy of note that the heat of neutralisation of very many organic acids of very varied constitution differs but little from the value + 13 cal. C. H. B.

Liquid Atmospheric Air. By S. v. WROBLEWSKI (*Ann. Phys. Chem.* [2], **26**, 134—144).—In many of its properties, atmospheric air resembles a perfectly homogeneous gas, and on compression it appears to the superficial observer to behave as a single gas, so that its critical pressure and temperature have been determined. But in this paper it is shown that the liquefaction of air is accompanied by various complex phenomena, resembling those noticed in the compression of a mixture of five volumes of carbonic anhydride with one of air. Thus if atmospheric air is compressed until the meniscus first formed disappears, and the pressure allowed to decrease slowly, there are produced two superposed menisci, separating heterogeneous fluids, in which the relative proportion of oxygen and nitrogen is different, the lower fluid containing about 21·3 per cent., the upper 17·5—18·5 per cent. oxygen. Secondly, the tension curves of atmo-

spheric air are not regular, inasmuch as on compression the temperature at first sinks uniformly in proportion to decrease of pressure, until a minimum point at — 198° is reached; on further compression the temperature begins to rise to a maximum at — 196°, and thence decreases. These irregularities of the tension curves show that the two constitutents of the air are not vaporised equally, and the temperature observed is dependent on the momentary composition of the fluid. V. H. V.

Variation of Temperature of Maximum Density of Water with Pressure. By G. P. Grimaldi (*Gazzetta*, **15**, 297—302).—Puschl and Van der Waals have shown that if the coefficient of compressibility of water decreases with increase of temperature, then the temperature of the maximum density of any liquid must decrease with increase of pressure. This point has been experimentally observed by Marshall, Smith and Ormond, and Tait. The last-named agree in assigning a decrease of one degree temperature for every increase of fifty atmospheres, whilst Van der Waals assigns a decrease of 3·24° under the same conditions. In this paper, it is pointed out that this value of Van der Waals is probably incorrect, inasmuch as it is based on wrong data of the coefficient of compressibility obtained by Grassi. V. H. V.

Do Crystals grow only by Juxtaposition of New Molecules? By L. Wulff (*Zeit. Kryst. Min.*, **10**, 374—389).—From his experiments the author concludes that in some cases at least this question must be answered in the negative.

Rate of Decomposition of Ozone. By E. Mulder (*Rec. Trav. Chim.*, **4**, 139—146).—In continuation of his experiments with the ozonometer described in a previous paper (*Rec. Trav. Chim.*, **3**, 137—157), the author finds that the rate of decomposition of ozone, in a mixture of ozone and oxygen, at a given temperature, is directly proportional to the number of ozone molecules present, and that this rate increases rapidly with the temperature. A. P.

Contact Actions in Dissociation. By D. Konowalow (*Ber.*, **18**, 2808—2833).—Wurtz in the course of investigation on vapour-densities found that in the case of amyl bromide, the time taken for the determination, other conditions remaining the same, affected the result. In a recent paper, the author in conjunction with Menschutkin observed that the nature of the substances with which the vapour came in contact influenced the degree of dissociation (Abstr., 1884, 1119), the phenomenon being very marked with fine asbestos. In this paper, the contact effect of various substances on the degree of dissociation of various amyl compounds is more fully examined, a slightly modified form of V. Meyer's vapour-density apparatus being used. Thus the contact of finely divided silica caused 53 per cent. of the vapour of tertiary amyl acetate to be dissociated at the end of 40 minutes. Amongst other substances, the following were found to be active in inducing this dissociation: silica, barium and calcium sulphates, animal charcoal, freshly cleaned platinum foil, glass wool and

glass powder from broken Rupert's drops. With amyl chloride, not only the pressure, &c., to which the vapour was subjected, but also the nature of the glass of the containing vessel, affected the degree of the dissociation. As regards the former, the collected results show that the velocity of the decomposition increases with increased pressure up to a certain point, at or above which it is independent of the pressure. As an explanation of this contact action phenomenon, it is asked whether it is not possible that the bombardment of the molecules on the solid matter causes the kinetic energy of the molecules to be transformed in part into the internal work required for their decomposition. However this may be, these phenomena herein detailed are analogous to those observed in the experiments of Faraday and Dulong, on the effect of finely divided substances in inducing the combination of hydrogen with oxygen, and other chemical changes.

In an added note, the author meets the criticisms of V. Meyer and Pond, and points out the reasons for the unsuccessful repetition of the experiments described by himself and Menschutkin.

V. H. V.

Decomposition of Carbon Compounds by the Electric Spark. By A. Pizzarello (*Gazzetta*, **15**, 233—238).—In this paper, a description is given of the decomposition of the vapours of various carbon compounds introduced into a Torricellian vacuum and subjected to a series of electric sparks. Thus under these conditions a given volume of methyl alcohol is tripled, owing to its resolution into carbonic oxide and hydrogen, thus: $CH_3{\cdot}OH = CO + 2H_2$; the presence of both these gases was indicated.

Similarly ethyl ether yields carbonic oxide, acetylene and hydrogen, together with carbon deposited on the platinum wires or walls of the tube, whilst ethyl formate gives water in addition to the above-mentioned products. V. H. V.

Dissociation of Salts containing Water, and Conclusions drawn therefrom as to the Constitution of the Salts. By W. Müller-Erzbach (*Chem. Centr.*, 1885, 470).—A continuation of the author's experiments in which the vapour-tension of the water in the salt is compared with that of pure water (Abstr., 1885, 952). In the present paper, the following salts are investigated:—$MgSO_4 + 7H_2O$, relative tension at $18 = 0{\cdot}34$, after loss of 1 mol. H_2O, relative tension $= 0{\cdot}009$; $NiSO_4 + 7H_2O$ = relative tension 0·56, became inappreciable after loss of 1 mol. H_2O; $CoSO_4 + 7H_2O$ gave similar results; $FeSO_4 + 7H_2O$ gave different results, according to the method of crystallisation, the normal results seemed to be relative tension at $18{\cdot}5 = 0{\cdot}36$; after loss of 3 mol. H_2O, inappreciable. $ZnSO_4 + 7H_2O$, relative tension at $19{\cdot}5° = 0{\cdot}43$; after loss of 5 mol. H_2O, this fell to 0·24—0·18, and was inappreciable when a salt containing $1\frac{1}{9}$ mol. H_2O was arrived at. Relative tension of $CuSO_4 + 5H_2O$ at $17° = 0{\cdot}04$—$0{\cdot}05$; of $CuSO_4 + 3H_2O$ = about 0·02; after long exposure over solid potash, a salt with $1\frac{2}{3}$ mol. H_2O was left. Relative tension of $MnSO_4 + 5H_2O = 0{\cdot}50$; of $MnSO_4 + 1\frac{1}{2}H_2O = 0{\cdot}003$; of $MnSO_4 + 1\frac{1}{8}H_2O = 0$: of $CaCl_2 + 6H_2O = 0{\cdot}12$; of $CaCl_2 + 4H_2O = 0{\cdot}08$; of $CaCl_2 + 2H_2O = 0{\cdot}013$—$0{\cdot}017$; of $CaCl_2 + H_2O = 0$: of $CoCl_2 +$

$6H_2O = 0{\cdot}20$; of $CoCl_2 + 4H_2O = 0$: of $MnCl_2 + 4H_2O = 0{\cdot}18$; of $MnCl_3 + 2H_2O = 0$: of $NaBr + 2H_2O = 0{\cdot}27$: of $BaCl_2 + 2H_2O = 0{\cdot}035$; of $BaCl_2 + H_2O = 0{\cdot}007$. The author calls attention to the peculiar behaviour of some salts, in which there is at first no loss of water, the tension then gradually rises until it attains its maximum.

A. J. G.

Diffusion of Fatty Alcohols and Acids. By A. Winkelmann (*Ann. Phys. Chem.* [2], **26**, 105—134).—This paper is an extension of the author's researches on the diffusion of homologous ethereal salts (Abstr., 1885, 10), and contains an account of similar experiments with the paraffinoïd alcohols and fatty acids. Observations with formic and acetic acids show that the observed reciprocal values of the molecular path-lengths are concordant with those calculated from the results of the ethereal salts; but in the case of the higher acids the calculated and observed values are not thus concordant. In the course of the research, it was noticed that in order to obtain comparable results, it was necessary to determine the tension of the vapour and its diffusion with equal quantities of the liquid.

The following table contains the diffusion coefficients and the mean path-lengths ($l \times 10^8$) in centimetres at 0° and 760 mm.

	Acetic acid.	Propionic acid.	Butyric acid.	Isobutyric acid.	Isovaleric acid.
Air	0·1061	0·8847	0·068	0·0704	0·0555
Hydrogen	0·404	0·3333	0·2639	0·2713	0·2118
Carbonic anhydride	0·0713	0·0595	0·0476	0·0472	0·0375
Mean path-length	297	227	166	171	124

Similar determinations were made with the paraffinoïd alcohols, and the deduced mean path-lengths of the molecules show considerable variation in the case of the higher alcohols, but with the lower these differences are more constant. Below are given some of the reduced results, the upper number giving that for air, the middle that for hydrogen, and the lower that for carbonic anhydride.

Alcohol.	Diffusion coefficient.			Mean path-length ($l \times 108$).
	Air.	Hydrogen.	Carbonic anhydride.	
Methyl	0·1325	0·5001	0·088	361
Ethyl	0·0994	0·3806	0·0693	259
Propyl	0·0803	0·3153	0·0577	203
Isobutyl	0·0688	0·2771	0·0483	168
Normal butyl	0·0681	0·2716	0·0476	164
Fermentation amyl	0·0585	0·234	0·0419	137
Normal amyl	0·0589	0·2351	0·0422	139
Normal hexyl	0·0499	0·1998	0·0351	111

In conclusion, the results obtained for molecular path-lengths by this diffusion method are compared with those by Meyer and Schumann's transpiration method (Abstr., 1881, 504); the latter gives values nearly double as great as the former. It is, however, shown that the tendency of the transpiration method is to give excessive results, and the apparent discrepancy is further cleared up by mathematical reasoning. V. H. V.

Conditions of Equilibrium in Aqueous Solutions. By T. Thomsen (*J. pr. Chem.* [2], **32**, 211—230).—Of the large number of substances which are now known to rotate the plane of polarisation of a ray of polarised light, sugar has been by far the most fully investigated. The optical activity of such substances is expressed as the *specific rotation* $[\alpha]$, which is calculated from the formula $[\alpha] = \frac{\alpha \cdot 100}{l \cdot c}$, where α = the observed rotation, l the length of liquid examined, and c the concentration (expressed in grams of active substance in 100 c.c.) of that liquid. If the liquid is a pure substance, c becomes 100 d, where d = sp. gr. (density compared with water at 4°); but if, as in the present case, the liquid is a solution of the active substance, c becomes $p \cdot d$ where p = the percentage of active substance in the solution, and the formula becomes $[\alpha] = \frac{\alpha \cdot 100}{l \cdot p \cdot d}$. The author points out the unfortunate looseness with which this formula is often used (p being, for instance, often confounded with c), and the fact that the kind of light used is often not stated, so that many determinations published are practically useless.

For cane-sugar the specific rotation has been found to be $[\alpha]_D = + 66{\cdot}5°$, and this value is correct within narrow limits, whatever the temperature or concentration of the solution employed. But in the case of most other optically active substances, the specific rotary power varies, and even sometimes changes in direction with change of temperature and concentration of solution. In the case of tartaric acid, the effect of heat and concentration is very marked, and, further, the rotation is increased between three and four fold by the neutralisation of the acid with an alkali. The author has taken advantage of this sensitiveness of tartaric acid in investigating the conditions of equilibrium in mixed solutions. He has observed the rotary power of 50, 40, 30, and 20 per cent. solutions of tartaric acid at the temperatures 10°, 20°, 30°, with the following results:—

p.	$t = 10°$.			$t = 20°$.			$t = 30°$.		
	d.	c.	$[\alpha]_D$.	d.	c.	$[\alpha]_D$.	d.	c.	$[\alpha]_D$.
50 p. c. ..	1·2745	63·725	+ 5·92°	1·2670	63·350	+ 7·36°	1·2600	63·000	+ 8·63
40 „ ..	1·2113	48·460	7·63	1·2065	48·260	8·95	1·2015	48·060	10·11
30 „ ..	1·1535	34·605	9·16	1·1495	34·485	10·41	1·1460	34·380	11·44
20 „ ..	1·0975	21·950	10·89	1·0945	21·890	11·99	1·0905	21·810	12·95

For each temperature, the variation curve for different degrees of concentration between 20 and 50 per cent. forms a straight line, and the following formulæ may therefore be deduced :—

$$[\alpha]_D^{10^\circ} = 14{\cdot}154 - 0{\cdot}1644p = -2{\cdot}286 + 0{\cdot}1644q.$$

$$[\alpha]_D^{20^\circ} = 15{\cdot}050 - 0{\cdot}1535p = -0{\cdot}300 + 0{\cdot}1535q.$$

$$[\alpha]_D^{30^\circ} = 15{\cdot}784 - 0{\cdot}1429p = +1{\cdot}494 + 0{\cdot}1429q.$$

The second set of formulæ are obtained from the first by taking $p = 100 - q$, where q = the percentage of water in the solution. It should be noticed, that whilst the variation for concentration, within the above limits, is constant, the increase of specific rotation for a given rise of temperature diminishes with increasing temperature. Taking this into account and using the above formulæ, the author has calculated the following more complete table :—

Specific Rotation $[\alpha]_D$ *of Tartaric Acid.*

p.	$t = 10°$.	$t = 15°$.	$t = 20°$.	$t = 25°$.	$t = 30°$.
50 p. c. ...	5·93°	6·67°	7·38°	8·03°	8·64°
40 „ ...	7·58	8·26	8·91	9·51	10·07
30 „ ...	9·22	9·85	10·45	10·99	11·50
20 „ ...	10·87	11·44	11·98	12·47	12·93

$$[\alpha]_D^{15^\circ} = 14{\cdot}615 - 0{\cdot}1588p = -1{\cdot}265 + 0{\cdot}1588q.$$

$$[\alpha]_D^{25^\circ} = 15{\cdot}429 - 0{\cdot}1480p = +0{\cdot}629 + 0{\cdot}1480q.$$

These results lie between those obtained by Krecke (*Arch. Néerlandaise*, **7**, 102) and those by Arndtsen (*Ann. Chim. Phys.* [3], **54**, 411).

The author finds that a solution of tartaric acid (50 per cent.) may be kept for months without undergoing any optical change.

Determinations of the rotary power of varying mixtures of tartaric and citric acids and water, tartaric and acetic acids and water, and tartaric and sulphuric acids and water were made. The results obtained lead to the conclusion that the two acids present appropriate water in the proportion in which they are present, or, in other words, that the solution consists of a mixture of solutions of the two acids of equal strength. Thus, for instance, if 30 grams tartaric acid and 20 grams citric acid are dissolved in 50 grams water, the tartaric acid will appropriate 30 grams, the citric 20 grams of this water, and the specific rotation of the tartaric acid will be that of a 50 per cent.

solution. In the case of sulphuric acid and tartaric acid, the former appears to be present in the shape of its hexahydrate, H_6SO_6. These results seem to show that from such observations, it will be possible to determine the state of hydration in which various substances exist in solution. L. T. T.

Molecular Movements. By G. Krüss (*Ber.*, **18**, 2586—2591).—Although the kinetic theory of gases gives some account of the translation of molecules through space, yet no satisfactory hypothesis has been brought forward to illustrate either the rotation of the molecules about their own axes, or the interatomic movements within the molecules. These two last the author classifies under the title of "*inner molecular movements.*" From the undulatory theory of light, deductions can be drawn regarding these molecular movements, inasmuch as the vibration of the ether, which fills the intramolecular space, is conditioned within that space by the velocity and amplitude of the molecular vibrations. Thus if λ be the wave-length of a ray emitted by a substance, v the velocity of light, the number of vibrations, n, which a molecule sends forth by movements of it as a whole and of its parts, can be determined by the equation $n = \frac{v}{\lambda}$. The phenomena of emission and of absorption spectra thus throws some light on the least and most extensive form of this inner molecular movement. In this paper, this latter point is discussed, together with its relation to the interatomic attraction, which is conditioned by the chemical constitution of the molecule; inasmuch as vibrations of the particles of a body are capable of being excited only by vibrations of a like period in the external ether, so from the wave-lengths of those rays of light, which are absorbed to the greatest degree by the solution of any substance, the number of the vibrations of the molecules within the liquid can be calculated from the equation above. These positions of greatest absorption for derivatives of indigo and fluoresceïn have previously been determined by the author (Abstr., 1883, 1042), and from the observations, results are obtained for the maximum number of vibrations for billionths of a second. In a table are given the results for indigo, its paraffinoïd-, bromo-, nitro-, and amido-derivatives, for rosolic acid and its tetrabromo-derivative, and for fluoresceïn and its potassium, bromo-, nitro-, and paraffinoïd-derivatives.

From the numbers given, it follows that the molecule of a compound emits fewer vibrations per second, the greater the number of hydrogen-atoms, or, *in the case of analogous replacements of the hydrogen-atoms, the increase or decrease of molecular vibrations is proportional to the number of hydrogen-atoms thus replaced.* The results are in accordance with those deduced by Kellstab from experiments on the transpirability of homologous compounds. V. H. V.

Simple Burner for Monochromatic Light. By Noack (*Chem. Centr.*, 1885, 497—498).—Consists of a hydrogen evolving apparatus, into the cork of which is inserted the stem of a Bunsen burner made of glass, and a wire for lowering or raising a block of metallic zinc. The salt for producing the required light is dissolved in the acid.

J. K. C.

An Aspirator. By A. Gawalovski (*Chem. Centr.*, 1885, 465).—A description of an aspirator, consisting of two vessels, revolving on an axis, and so constructed that it can be used as an aspirator or respirator. P. P. B.

New Apparatus for Chemical Laboratories. By A. Kalecsinszky (*Chem. Centr.*, 1885, 545—546).—To expel sulphuric acid in the course of analysis, the author employs a wide glass tube sealed at the lower and upper extremities, the upper end being driven inwards to receive a platinum crucible fitted in with asbestos, and having a small open tube inserted laterally. Through this tube sulphuric acid is passed into the apparatus; the tube is connected with a suitable condenser, heat applied, and the liquid contents of the platinum crucible speedily evaporate. The author also describes a simple apparatus for obtaining an air blast by means of air and water dropping into a large flask. J. K. C.

Improved Method of Ventilating Laboratories. By C. M. Stuart (*Chem. News*, **52**, 208).—A modification of the glass hood described by Hempel (*Ber.*, **18**, 1437), so arranged as to be placed on every working bench.

A Gas Regulator constructed without Metal. By H. Schiff (*Ber.*, **18**, 2833—2841).—The arrangement cannot well be described without a figure.

Inorganic Chemistry.

Source of Hydrogen Occluded by Zinc-dust. By G. Williams (*Chem. News*, **52**, 205—207).—In continuation of the experiments on the occlusion of hydrogen by zinc-dust (comp. Abstr., 1885, 369, 634), it is now shown that when 6·749 grams (1 c.c.) of commercial zinc-dust was exposed for a long time in a hard glass retort to the greatest heat of a Bunsen burner, it yielded as much as 47·4 c.c. of hydrogen. When the zinc-dust was moistened with boiling water and dried at 100°, its weight increased by about 0·1742 gram on 6·479 grams, and on heating 6·479 grams of this dried dust in the manner described above, 89·4 c.c. of hydrogen were obtained; whilst zinc-dust, which had been exposed in a moist atmosphere until it ceased to gain in weight, then dried and heated as in the other experiments, gave as much as 362·8 c.c. of hydrogen per 6·479 grams of zinc-dust. Hence zinc-dust takes up water and decomposes it, and gives up its hydrogen on heating; in another experiment it was proved that zinc-dust absorbs hydrogen (9 c.c. per 6·479 grams) at ordinary temperatures, when surrounded by it in a moist condition. The author's previous conclusions (*loc. cit.*), therefore, are confirmed. D. A. L.

Genesis of Sulphur Crystals in Square Tables. By C. Brame (*Compt. rend.*, **101**, 639—642).—A description of peculiar crystals obtained by condensing sulphur vapour on glass plates.

Iodide of Nitrogen. By F. Raschig (*Annalen*, **230**, 212—221).—The author accounts for the discordant results of the analyses of iodide of nitrogen by Gladstone (this Journal, 1851, 34), Stahlschmidt (*Pogg. Ann.*, **119**, 421), and Bunsen (*Annalen*, **84**, 1) by the fact that the precipitate obtained by adding ammonia to a solution of iodine, is decomposed by washing with water. Sesqui-iodamine, NH_3,NI_3 or NH_2I,NHI_2, is first precipitated, but it is converted during the process of washing into NHI_2 and NI_3. The latter compound dissolves in potassium cyanide, forming cyanogen iodide:—$NI_3 + 3KCN + 3H_2O = 3CNI + NH_3 + 3KOH$. The iodide of nitrogen prepared from a solution of iodine differs in its properties from the iodide obtained by the action of ammonia on finely divided iodine. The latter compound is much more explosive than the former, as it is capable of exploding when moist. The composition of this substance has not yet been ascertained. W. C. W.

Behaviour of Carbonic Anhydride towards Hydrogen at a High Temperature. By A. Naumann and C. Pistor (*Ber.*, **18**, 2724—2727; comp. this vol., p. 1036).—Hydrogen has no reducing action on carbonic anhydride at 900°.

Reactions with Carbonic Anhydride, Carbon Bisulphide, and Sulphurous Anhydride. By A. Eiloart (*Chem. News*, **52**, 183—184).—When a mixture of carbonic anhydride and carbon bisulphide vapour is passed over copper heated to redness, almost pure carbonic oxide is abundantly evolved with simultaneous formation of copper sulphide, Cu_2S. Carbon bisulphide alone is decomposed when passed over copper heated below redness, and if copper, coated with carbon from the decomposition of carbon bisulphide, is heated in a stream of carbonic anhydride, only a limited and small quantity of carbonic oxide is slowly produced. Hence the mixture of gases is necessary for the above reaction, and decomposition and combination evidently go on at the same time. Without copper the mixture of gas is not decomposed in this manner, for instance, when passed over heated pumice. Sulphurous anhydride and carbon bisulphide, when passed over copper or pumice heated even below redness, give rise to carbonic anhydride, and as a secondary product carbonic oxide. When sulphurous anhydride is passed over strongly heated carbon, freed as far as possible from air and hydrogen, sulphur is deposited and carbonic anhydride formed. D. A. L.

Absorbents for Carbon Bisulphide Vapour. By A. Eiloart (*Chem. News*, **52**, 184).—To test the efficiency of various absorbents for carbon bisulphide vapour, air saturated with this vapour was passed through certain substances, at the rate of 1 litre per hour. Caoutchin, powdered roll sulphur, bromine dissolved in potassium bromide, and linseed oil are imperfect absorbents, iodine and potassium

tri-iodide absorb completely a large proportion of carbon bisulphide vapour, but soon get saturated. When these substances are used, a guard tube (filled with paraffin) must be attached to arrest iodine vapour. The carbon bisulphide can be removed from the saturated iodine solution by simple exposure to the air. Large quantities of gas cannot be conveniently treated in this manner. For analytical purposes, the volume of gas to be analysed is treated with linseed oil in a Crum's tube; used in this way, linseed oil is the best, as it absorbs the carbon bisulphide immediately without dissolving the carbonic anhydride.

D. A. L.

Artificial Formation of Twin Crystals of Potassium Sulphate and Chromate by Increase of Temperature. By H. Baumhauer (*Zeit. Kryst. Min.*, **10**, 405).—The observation made by Mallard, that in twin crystals of potassium sulphate new twin-lamellæ are formed by heating, is confirmed by the author. Perfectly simple crystals can, by heating, be converted into complicated twin crystals. In the same way, plates of potassium chromate, cut parallel to the basal plane, after slight heating, exhibit a great number of twin lamellæ.

B. H. B.

Action of Sodium Thiosulphate on Metallic Salts. By P. Jochum (*Chem. Centr.*, **16**, 642—644).—By treating solutions of sulphate or chloride or acetate of copper, lead, cadmium, silver, gold, platinum, zinc, manganese, cobalt, or nickel, with solution of sodium thiosulphate, the author has obtained a series of double thiosulphates, of which an account is given in this paper. P. P. B.

Action of Carbonic Oxide on Lead and Silver Chlorides. By A. G. Bloxam (*Chem. News*, **52**, 183).—Contrary to the statement of Göbel (*J. pr. Chem.*, **6**, 388), who describes a method of preparing carbonyl chloride founded on the supposed reaction between carbonic oxide and these chlorides, the author finds that neither lead nor silver chloride is attacked by heating in a current of dry carbonic oxide. When heated in a current of moist nitrogen, lead chloride loses weight with evolution of hydrogen chloride. D. A. L.

Alteration of Mercurous Iodide by Exposure to Light. By — Yvon (*J. Pharm.* [5], **11**, 148—149).—Crystallised mercurous iodide, exposed to the light for eight years, in a flask closed by a sheet of paper, had become almost black. Analysis shows the altered iodide to contain 60·72 per cent. of mercury, instead of 61·16 per cent.

J. T.

Chromic Phosphate. By C. L. Bloxam (*Chem. News*, **52**, 194—195).—The precipitate produced by boiling solutions of chromic salts with sodium phosphate and acetic acid has been found by the author to consist of normal chromic phosphate, mixed with slight excess of chromic oxide, Cr_2O_3, and retaining about 5 mols. H_2O at 100°. D. A. L.

Molybdenum-derivatives. By C. Bärwald (*Chem. Centr.*, 1885, 424—425).—Some time ago, Werther showed (*J. pr. Chem.*, **83**, 198) that hydrogen peroxide caused a yellow coloration in acid solutions of

molybdic acid. The same reaction takes place with the oxides, sulphides, and salts of molybdenum, but after a time gas is evolved, and the colour disappears. The reaction forms a good test for molybdenum, and serves to detect it in the presence of chromates, as the blue coloration caused by hydrogen peroxide with chromates may be extracted by agitation with ether, whilst the yellow molybdic coloration remains in the aqueous liquid. The test is, however, much less delicate with molydic compounds than with chromates, and is quite masked by the presence of vanadium or titanium compounds.

The normal molybdates and polymolybdates when added to hydrogen peroxide cause a brown coloration and strong evolution of oxygen. But when commercial ammonium molybdate, $Am_6Mo_7O_{24} + H_2O$, or analogous salts (for instance, Rammelsberg's seven-thirds salts) are employed, scarcely any evolution of gas takes place, and the deep yellow solutions yield crystalline lemon-yellow compounds by spontaneous evaporation. The ammonia compound,

$$18MoO_3,14NH_3,3H_2O_2 + 18H_2O,$$

crystallises in lemon-yellow prisms which do not change on exposure to the air. Acids deepen the yellow colour of the solution, alkalis discharge it. If zinc is added to the acidified solution, it becomes darker and finally green. Potassium ferrocyanide and thiocyanate give the same reactions as with ordinary molybdates; lead nitrate gives a white precipitate, soluble in nitric acid, insoluble in, but becoming dark-coloured by ammonia. Silver and mercurous nitrites both give white precipitates; barium chloride, a white compound, $19MoO_3,8BaO,2H_2O_2 + 13H_2O$; ferrous sulphate, a dark yellow voluminous precipitate. Silver nitrate gives a pale yellow amorphous precipitate, $32MoO_3,13Ag_2O,2H_2O_2$. Ferric sulphate yields an amorphous lemon-coloured powder, $Fe_2O_3,5MoO_3,16H_2O$. When fused with molybdic acid the ammonia compound yields a violet-blue powder of the formula Mo_3O_8. The crystals of the ammonia compound are highly refractive, and have a sp. gr. of 2·975; the sp. gr. of their solution saturated at 17·4° is 1·486.

The analogous potassium molybdate, $K_6Mo_7O_{24} + 4H_2O$, yields, with the peroxide, the derivative $16Mo_3O,6K_2O,4H_2O_2 + 13H_2O$; no corresponding sodium salt could be obtained.

The author has also made experiments on the use of the electrolytic method for the quantitative estimation of molybdenum, but finds the results unsatisfactory. L. T. T.

Vanadic Anhydride. By A. Ditte (*Compt. rend.*, **101**, 698—702). —When ammonium vanadate is heated in a closed crucible out of contact with air, the vanadic acid is reduced by the evolved gases, and yields a dark coloured mixture of the two oxides, V_2O_4 and V_2O_3, in which the latter predominates. If this product is oxidised with nitric acid, the solution evaporated to dryness, and the residue gently heated, pure vanadic anhydride is left in the form of a reddish-yellow ochreous powder. When this powder is exposed to the air, it absorbs water and becomes red, forming first the hydrate V_2O_5,H_2O, and afterwards the hydrate $V_2O_5,2H_2O$. The latter compound, if placed in an

atmosphere saturated with aqueous vapour, absorbs more water and forms the hydrate $V_2O_5,8H_2O$, but this loses 6 mols. H_2O when exposed to the air. The amount of water absorbed by the vanadic anhydride depends on the tension of the aqueous vapour in the surrounding atmosphere. When the anhydride or one of the red hydrates is brought in contact with a small quantity of water, it instantly forms a viscous, almost gelatinous mass, which dissolves completely on adding more water, forming a deep blood-red, limpid solution. No precipitate is formed when this solution is boiled, or if it is mixed with alcohol in the cold, but the addition of a small quantity of nitric acid produces a flocculent reddish precipitate soluble in excess of acid with production of a straw-coloured solution. If this solution is evaporated in a vacuum over potash, it leaves a reddish, velvety mass of hydrated vanadic acid, readily soluble in water with production of the original blood-red solution.

If the blood-red solution is mixed with excess of potassium chloride, the whole of the vanadic anhydride is precipitated in reddish flocks, which are not altered by boiling, and are insoluble in water containing potassium chloride, but dissolve slightly in pure water, forming a yellow solution, whilst the precipitate, which settles very slowly, becomes orange coloured.

When a cold solution of ammonium vanadate is mixed with a small quantity of nitric acid, a reddish turbidity is produced, which disappears on adding more acid, but if the solution is boiled, the greater part of the vanadium is precipitated. This precipitate, after washing, and drying by exposure to air, has the composition $V_2O_5,2H_2O$, but differs from the hydrate described above, in that it does not alter in contact with water, and is only very slightly soluble even at 100°.

If the product of the calcination of ammonium vanadate is heated in a current of dry air at 440° for several hours, it is converted into a pale yellow vanadic anhydride with a slight greenish tinge. This variety corresponds with the slightly soluble hydrates, and can also be obtained by heating these hydrates at 350—440°, but is then reddish-yellow. It does not absorb moisture from the air, and dissolves only very slightly in water, forming a yellow solution.

When ammonium vanadate is heated in contact with the air until the residue fuses, the product is not pure vanadic anhydride, but contains a compound of this oxide with the lower oxide, V_2O_4. If, however, the product obtained by the action of nitric acid on the mixed oxides formed by heating ammonium vanadate in a closed vessel, is heated to fusion and allowed to cool, it solidifies in dark brownish-red needles, which have a greasy lustre and are transparent in thin plates. This variety of the anhydride does not form a hydrate even if left in contact with water for several months, and a saturated solution of it contains only 0·05 gram per litre.

From these observations, it follows that vanadic anhydride exists in three distinct modifications, which may be regarded as analogous to the polymeric varieties of phosphoric anhydride, described by Hautefeuille and Perrey. C. H. B.

Action of Hydrogen Peroxide on Antimony Sulphides. By F. Raschig (*Ber.*, **18**, 2743—2745).—When freshly precipitated antimony sulphide, from 30 grams of tartar emetic, is treated with 500 c.c. of concentrated ammonia, and 900 c.c. of a $2\frac{1}{2}$ per cent. solution of hydrogen peroxide, about $\frac{1}{6}$ is converted into antimonic acid which forms a flaky precipitate. The solution contains ammonium sulphate and antimoniate; the latter salt is precipitated by the addition of alcohol, and when dried at the ordinary temperature, has the composition $NH_4SbO_3 + 3H_2O$, and is therefore identical with Frémy's hydrogen ammonium metantimoniate, $H_2(NH_4)_2Sb_2O_7 + 5H_2O$. The reaction above described is fresh evidence of the non-existence of an antimonic acid corresponding with orthophosphoric acid.

N. H. M.

Equilibrium in the Reaction of Hydrochloric Acid on Antimony Trisulphide, and of Hydrogen Sulphide on a Solution of Antimony Trichloride. By J. Lang (*Ber.*, **18**, 2714—2724).—Experiments made by the author confirm the result obtained by De Clermont and Frommel (Abstr., 1879, 13), that water decomposes antimony trisulphide; the decomposition continues as long as water is present.

Hydrochloric acid of all degrees of strength acts on antimony sulphide. In presence of an excess of the sulphide, the action continues until the strength of the hydrochloric acid diminishes to a certain point, this point depending on the amount of hydrogen sulphide present in the solution. The equilibrium will then be disturbed if the pressure on the hydrogen sulphide over the solution be increased; this causes a reversal of the reaction which is shown by the separation of antimony sulphide. On the other hand, if the hydrogen sulphide be removed from the solution as it is formed, the action of the hydrochloric acid will continue until all the antimony sulphide is dissolved.

N. H. M.

Mineralogical Chemistry.

Absolute Hardness of Minerals. By F. Pfaff (*Zeit. Kryst. Min.*, **10**, 528—531).—The author has made a series of experiments to determine the absolute hardness of minerals. An accurate chisel-shaped diamond cutter was passed with constant pressure in the same direction 100 or 1000 times over the face of the crystal, and the volume thus removed estimated by weighing the crystal before and after the experiment. A detailed description is given of the instrument employed. Assuming that the hardness of two crystal planes is in inverse proportion to the volume of material removed, with the same load and the same number of passings to and fro of the diamond over an equal area, the hardness of minerals can then be expressed numerically, a given substance (talc) being taken as unit.

B. H. B.

The Gold Beds of Mount Morgan, Queensland. By R. L. JACK (*Dingl. polyt. J.*, **258**, 45).—These beds are situated about 35 kilos. south-south-west of Rockhampton. The gold is distributed in hæmatite ironstone and in siliceous sinter. D. B.

Copaline from Hütteldorf, near Vienna. By G. STARKL (*Zeit. Kryst. Min.*, **10**, 427).—In the slate of the Vienna sandstone, a fossil resin occurs in sharply angular fragments, or in small grains of 8 mm. diameter. Its colour varies between light greenish-yellow and brown. It is transparent to translucent. Several grains exhibit distinct fluorescence. Its density is less than 1·1. It is brittle, fuses at 160 to 165° to a clear liquid; at 360° it becomes brownish-black, hard, with metallic lustre, and at a red heat it burns leaving no residue. B. H. B.

Pseudomorphs. By E. DÖLL (*Zeit. Kryst. Min.*, **10**, 423).—The author describes pseudomorphs of iron pyrites after copper pyrites, from Kapnik, and pseudomorphs of tetrahedrite after copper pyrites, from Felsöbánya.

In the pseudomorphs from Kapnik and Felsöbánya described, and in the pseudomorphs of iron pyrites after copper pyrites from Müsen, numerous spherical cavities were observed, around which the iron pyrites is grouped. This the author regards as a characteristic structure for many pseudomorphs. B. H. B.

Galena with Octahedral Cleavage from Wermland. By H. SJÖGREN (*Zeit. Kryst. Min.*, **10**, 507—508).—In a specimen of galena from Nordmarks mines in Dr. Lundström's collection, the usual cubical cleavage is not developed. On breaking up the specimen irregular fragments are formed of a distinctly octahedral character. The ordinary cubical cleavage is developed after two hours' heating at 200°; at 250° much more rapidly; and at 300° with still greater facility. Analysis gave the following results :—

Pb.	Bi.	Ag.	Fe.	S.	Total.
85·67	0·76	0·05	0·39	13·59	100·46

The author is of opinion that the percentage of bismuth sulphide, which was also observed in the galena of Habach, may be the cause of the octahedral cleavage of galena. The galena, with octahedral cleavage, from Mt. Blanc, described by A. Brun (Abstr., 1883, 428), also gave on analysis 1 per cent. of bismuth sulphide.

B. H. B.

Tetrahedrite from the Alaska Vein, Colorado. By T. LIWEH (*Zeit. Kryst. Min.*, **10**, 488—489).—The author has examined crystals of the new mineral from the Alaska vein, S.W. Colorado, described by König under the name of alaskite (*Zeit. Kryst. Min.*, **4**, 42), in order to prove crystallographically whether the mineral really belongs to the isomorphous rhombic group of copper-bismuth glance, lead-arsenic glance, &c. The measurements, however, showed the crystals to belong to the regular system; the mineral being evidently

tetrahedrite. A qualitative analysis showed the presence of S, Bi, Sb, Pb, Ag, Cu, Zn, the elements given by König in his analysis of alaskite. The following forms were observed on the crystals: $+\frac{O}{2}$, $+\frac{2O2}{2}$, $\infty O\infty$, ∞O, $-\frac{2O2}{2}$, $-\frac{4O4}{2}$, $+\frac{\frac{3}{2}O}{2}$, $-\frac{O}{2}$. B. H. B.

Microscopic Character of Variegated Copper Ore from New Mexico. By H. Baumhauer (*Zeit. Kryst. Min.*, **10**, 447—450).—The author has examined, under the microscope, a specimen of bornite from Chloride, in New Mexico. He found that the compact bornite was of a crystalline character, with inclusions of copper glance. On treating these inclusions with concentrated nitric acid, it was seen that they consisted of a number of separate crystals, irregularly grouped together. In addition to copper glance, a second mineral was observed here and there in the inclusions. This might possibly be galena. Small patches of copper pyrites also occasionally occur in the inclusions. In several places, the ore incloses small distinctly developed crystals of quartz. B. H. B.

Antimonite from Czerwenitza. By H. v. Foullon (*Zeit. Kryst. Min.*, **10**, 429).—Antimonite occurs in the red trachytic mother-rock of the opals, in the form of hemispherical radiated aggregates, 1 cm. in diameter. These are frequently covered with hyalite. Several of the hemispherical aggregates of antimonite consist exclusively of antimonite fibres; others, however, are found on microscopic examination to consist of antimonite with interstratified hyalite, which the author regards as pseudomorphs after antimonite. Similar pseudomorphs are found at the Josephis adit, in Klausenthal, near Eperies. B. H. B.

Selenides from the Andes. By F. Heusler and H. Klinger (*Ber.*, **18**, 2556—2561).—Analysis of zorgite containing a considerable quantity of silver. The substances are not homogeneous; analysis of the different parts gave—

	Ag.	Cu.	Pb.	Co.	Bi.	Se.	Total.
I....	19·20	12·43	35·70	traces	—	32·77	100·09
II....	27·49	25·40	17·10	0·39	—	29·54	99·92
III....	15·87	36·15		1·73		46·25	100·00
IV....	19·16	35·77		3·45		41·62	100·00

I and II clear bluish-green substance of silvery lustre. I agrees with the formula $Ag_2Se,2PbSe,2CuSe$. III and IV, darker samples of bluish lead colour, are essentially selenides of silver and copper (comp. Pisani, Abstr., 1880, 440). A. J. G.

Refractive Indices of Fluorspar. By E. Sarasin (*Zeit. Kryst. Min.*, **10**, 523—524).—The author has determined the refractive indices of a fluorspar prism, with a refraction angle of 60° 4′ 55″. A table of the results is given for the spectrum lines, A, *a*, B, C, D, F, *h*,

H, (Cd) 9, 10, 11, 12, 17, 18, 23, 24, 25, 26, (Zn) 27, 28, 29, (Al) 30, 31, 32. B. H. B.

Optical Properties and the Micro-structure of Corundrum. By A. v. Lasaulx (*Zeit. Kryst. Min.*, **10**, 346—365).—Corundum is without doubt an optically uniaxial mineral crystallising in the hexagonal system. Disturbances in the regular optical behaviour depend on the nature of the growth and the structure of the corundum crystal. The crystals occurring in volcanic rocks appear, as a rule, to have a more uniform constitution and a more regular optical behaviour than those found in the older crystalline rocks. The optical disturbances appear throughout to be connected with the more or less distinctly developed structural faces parallel to R, ∞P2, and 0R. The concentric structure in the direction of one or other of these planes determines the cleavage, which is developed in the direction of R alone, or R and 0R, or ∞P2 and 0R, or all three planes at the same time, more or less perfectly. The cleavage is not dependent on the twin lamellæ present, but on the other hand the latter are dependent on the presence of the structural planes which determine the cleavage. But both appear simultaneously almost always. In this case, structural and twin planes are identical. In the direction of ∞P2, the plane of symmetry, a twin formation is not possible; in the direction of 0R it is entirely unknown. The optical disturbances in the zone lamellæ bounded by the structural planes are, however, of two kinds: —1. Optical disturbance is effected by tension in the zones of the crystal. 2. It occurs in consequence of interpolated twin lamellæ. Lastly, optical disturbances also occur in corundum crystals, in consequence of processes of alteration, producing granular, laminated, or fibrous products in the interior of the crystals. In this case, however, a regular interference figure is not exhibited. B. H. B.

Corundum in Graphite. By H. Wichmann (*Zeit. Kryst. Min.*, **10**, 429).—On the surface of the graphite of Mühldorf, near Spitz, in Lower Austria, small crystals of corundum occur. The crystals attain a thickness of 0·5—6 mm., and a length of 7—25 mm. They are of a red to blue colour, rarely grey, but always clouded with inclusions. The translucent crystals prove to be biaxial, with a rather large axial angle. B. H. B.

Gahnite and Epidote from Rowe, Massachusetts. By A. G. Dana (*Zeit. Kryst. Min.*, **10**, 490—492).—With iron pyrites, copper pyrites, and quartz, the author found at Davis' mine, Rowe, fragments of gahnite, which on analysis gave the following results:—

Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	ZnO.	SiO_2.	Total.	Sp. gr.
54·83	3·00	3·37	trace	1·93	36·92	0·53	100·58	4·53

The following minerals also occur associated with the gahnite:—Ilmenite, apatite, rutile, sphalerite, garnet, calcite, green crystals of a triclinic felspar, and epidote. The epidote occurs in short prisms, opaque, and of a greenish-grey colour. Analysis gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	MgO.	CaO.	Alkalis.	H_2O.	Residue.	Total.
38·20	24·62	12·20	0·57	0·13	21·59	0·37	2·16	0·35	100·19

B. H. B.

Goethite from Pitkäranta in Finland. By M. Weibull (*Zeit. Kryst. Min.*, **10**, 511—512).—The author describes specimens of quartz and fluorspar with cavities lined with rock crystal and hæmatite, on which needles and radiated aggregates of goethite were crystallised out. An analysis of the goethite gave 89·65 per cent. of ferric oxide, and 10·50 per cent. of water. The mineral is therefore a very pure goethite. B. H. B.

Zircon in Stratified Rocks. By F. Sandberger (*Zeit. Kryst. Min.*, **10**, 405).—The author has observed transparent crystals of zircon in the granite of Schapbach, in the Black Forest, of Windeck, near Weinheim, of Heidelberg, Ilmenau, of the Luisenburg, near Wunsiedel, Nabburg and Wörth, near Regensburg. The crystals exhibit exclusively the combination $\infty P\infty$. Transparent zircons are also found in gneiss and mica-diorites, and in the porphyry of the Wagenberg, near Weinheim. Microscopically small zircons of the same form are widely distributed in the sedimentary rocks, the material of which is mainly derived from the older rocks; for example, in the variegated sandstones of the Black Forest and Spessart, in carboniferous sandstone, in the Upper Keuper sandstone, and in the sands of the Valley of the Maine. B. H. B.

Boracite. By H. Baumhauer (*Zeit. Kryst. Min.*, **10**, 451—457).—The author brings forward further arguments to prove that boracite at the ordinary temperature, in the state in which it is met with in nature, does not crystallise in the regular, but in the rhombic system. B. H. B.

Uranothallite. By A. Brezina (*Zeit. Kryst. Min.*, **10**, 425—426).—Crystals of uranothallite recently obtained at Joachimsthal, gave, for the rhombic crystals, the axial ratio $a : b : c = 0{\cdot}954 : 1 : 0{\cdot}783$. The analysis gave the following results:—

UO_2.	CO_2.	CaO.	FeO.	H_2O.	Total.
35·45	23·13	16·28	2·48	22·44	99·78

corresponding with the formula $2CaCO_3 + UC_2O_6 + 10H_2O$.

B. H. B.

Occurrence of Hornstone and Barytes in the Porphyry District of Teplitz. By G. Laube (*Zeit. Kryst. Min.*, **10**, 421).—In a description of a crystal of barytes from Teplitz, in Bohemia (*Zeit. Kryst. Min.*, **9**, 221), Becke stated that the crystal was deposited from the Teplitz mineral water, which, according to the analyses of Sonnenschein, contains no barytes. This statement the author corrects by showing that barytes occurs in mineral spring fissures only where they traverse the Cenomanian hornstone-conglomerate occurring in the neighbourhood of Teplitz. From these fissures honey-yellow crystals of barytes have been long known. The Teplitz springs, however, do not contain barium. Only in the Neubad spring have

traces of barium been found. This spring passes through hornstone-conglomerate containing barytes. B. H. B.

Halotrichite and Epsomite from the Falu Mine. By M. Weibull (*Zeit. Kryst. Min.*, **10**, 512).—In two portions of the Falu mine, where the degree of moisture is low, and the temperature relatively high, sponge-like masses occur of a recent mineral, which appears to be a mixture of epsomite and halotrichite. The sp. gr. of the mixture is 1·77. The analysis gave results corresponding with the formula—

$$2(MgSO_4 + 7H_2O) + (FeZnCa)(AlFe)_2(SO_4)_4 + 22H_2O.$$

B. H. B.

Turquoise from Nischapur in Persia. By E. Tietze (*Zeit. Kryst. Min.*, **10**, 428).—The mother-rock of the turquoise of Nischapur is, contrary to all former descriptions, a porphyritic trachyte. In this, and in a breccia formed of angular fragments of the trachyte, the turquoise occurs in veins, 2 to 6 mm. thick, or in irregular patches. In the trachyte, pseudomorphs of turquoise after orthoclase occur. Turquoise is also found in shapeless fragments in the alluvium in the neighbourhood of the trachyte rocks. B. H. B.

Berzeliite. By L. J. Igelström (*Zeit. Kryst. Min.*, **10**, 516—517).—The author notes the discovery of berzeliite, hitherto found only at Långban, at the Moss mine in Wermland. An analysis gave the following results:—

As_2O_5.	CaO.	MgO.	Mn, Pb and Cl.
57·80	25·25	16·95	traces

This corresponds with Dana's formula for berzeliite—

$$(CaMgMn)_{10}As_8O_{25}.$$

B. H. B.

Xanthoarsenite, a New Mineral from Oerebro. By L. J. Igelström (*Zeit. Kryst. Min.*, **10**, 518—519).—The new mineral occurs at a small iron mine 6 miles east of Grythytta. Its colour is sulphur-yellow to orange. In thin splinters, it is translucent. Before the blowpipe, it melts to a black glass, giving a strong odour of arsenic. Analysis gave the following results:—

As_2O_5.	MnO.	FeO.	MgO.	CaO.	H_2O.
33·26	43·60	3·11	6·08	1·93	12·02

B. H. B.

Manganostibite, a New Mineral from Wermland. By L. J. Igelström (*Zeit. Kryst. Min.*, **10**, 519).—This mineral occurs at the Moss mine, in small, black, rhombic crystals. An analysis of 0·54 gram gave the following results:—

Sb_2O_5.	As_2O_5.	MnO.	FeO.	CaO.	MgO.	Total.*
24·09	7·44	55·77	5·00	3·62	3·00	99·92

B. H. B.

* The figures given only add up to 98·92.

Vanadates and Silver Iodide from New Mexico. By F. A. Genth and G. v. Rath (*Zeit. Kryst. Min.*, **10**, 458—474).—Quite recently new workings at the Sierra Grande Mine, Lake Valley, Donna Anna Co., New Mexico, have yielded a number of highly interesting and rare minerals, which have been examined chemically by F. A. Genth, and crystallographically by G. v. Rath.

Vanadinite, from the Sierra Bella Mine, Lake Valley, gave the following results on analysis:—

	Cl.	P_2O_5.	V_2O_5.	As_2O_5.	PbO.	Total.*	Sp. gr.
I....	2·39	0·57	17·37	0·24	79·43	100·00	—
II....	2·49	0·39	17·44	1·33	78·31	100·26	6·862

II is the analysis of vanadinite from the Sierra Grande. This corresponds with the formula $Pb_5Cl[(VAsPb)O_4]_3$; whilst analysis I gives a small excess of lead, probably present as cerussite.

Lead Arsenio-vanadate—Endlichite.—An analysis of a supposed vanadinite from the Sierra Grande gave the following results:—

SiO_2.	Fe_2O_3.	CaO.	Cl.	As_2O_5.	V_2O_5.	PbO.	CO_2,H_2O.	Total.
76·44	0·99	0·30	0·44	2·16	1·60	15·94	[2·13]	100·00

The mineral has thus the composition of equal mols. of mimetite and vanadinite: $Pb_5Cl(AsO_4)_3 + Pb_5Cl(VO_4)_3$. This mineral the authors believe to be new, and propose for it the name of endlichite, after the director of the Lake Valley mines.

Descloizite.—Very fine red and brown crystals have recently been found at the Sierra Grande. The mean results of three analyses of the red (I), and of three analyses of the black variety (II) gave the following results:—

	PbO.	CuO.	ZnO.	MnO.	FeO.	As_2O_5.	V_2O_5.
I	56·12	1·10	17·41	0·49	0·15	0·20	21·65
II	56·36	0·87	13·91	2·74	0·30	0·50	21·35

	P_2O_5.	H_2O.	Total.	Sp. gr.
I	—	2·37	99·49	6·106
II	0·04	3·39	99·46	5·848

After subtracting the impurities shown by the black descloizite, its analysis agrees very well with that of the pure red, the composition being expressed by the following formula:—

$$Pb_2(HO)(V,As,P)O_4 + (Zn,Mn,Cu,Fe)_2(HO)(V,As,P)O_4.$$

No indunium is present in the vanadates of Lake Valley.

On the new descloizite crystals, the following forms were observed:—P, $2\breve{P}2$, $\frac{3}{2}\breve{P}3$, $\frac{1}{2}\breve{P}\infty$, $2\breve{P}\infty$, ∞P, $\infty\breve{P}3$, $\infty\breve{P}\infty$, $\infty\breve{P}\infty$, 0P, with the rhombic axial ratio, $a : b : c = 0{\cdot}6367 : 1 : 0{\cdot}8046$.

Silver iodide.—Pure silver iodide is frequently found accompanying the vanadates of the Sierra Grande. It occurs with calcite and red descloizite in yellow, indistinct crystals and crystalline masses; and with vanadinite and black descloizite in very small, indistinct, rounded crystals. B. H. B.

* The figures given only add up to 99·96.

Minerals of the Pegmatite Vein at Moss. By W. C. Brogger (*Zeit. Kryst. Min.*, **10**, 494—496).—The author gives a long list of the minerals occurring in the pegmatite vein at Moss, the remarks on the new mineral *anneródite* being of special interest. This mineral is black with metallic to resinous semi-metallic lustre. H. = 6; sp. gr. 5·7. Analysis gave the following results:—

Nb_2O_5.	SnO_2.	SiO_2.	ZrO_2.	UO_2.	ThO_2.	Ce oxides.	Y oxides.	PbO.
48·13	0·16	2·51	1·97	16·28	2·37	2·56	7·10	2·40

FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	Al_2O_3.	H_2O.	Total.
3·38	0·20	3·35	0·15	0·16	0·32	0·28	8·19	99·51

corresponding with the formula

$$2R_2Nb_2O_7(+ 5H_2O + \tfrac{1}{2}SiO_2).$$

The mineral, therefore, resembles samarskite, from which it differs crystallographically. The axial ratio is rhombic; $a : b : c =$ 0·40369 : 1 : 0·36103. The forms observed were, $\infty\breve{P}\infty$, $\infty\breve{P}\infty$, 0P, ∞P, $\infty\breve{P}3$, $\infty\breve{P}5$, $2\breve{P}\infty$, $\frac{1}{2}\breve{P}\infty$, $\breve{P}\infty$, P, $2\breve{P}2$, $2\breve{P}2$, $3\breve{P}3$, 2P.

B. H. B.

Quartz from Burke, North Carolina. By G. v. Rath (*Zeit. Kryst. Min.*, **10**, 475—487).—A description of peculiar crystals from this locality.

Opal from Nagasaki, Japan. By H. Sjögren (*Zeit. Kryst. Min.*, **10**, 508).—The mineral is of a yellowish-brown to chesnut-brown colour, and possesses the usual characteristics of opal. Under the microscope, no trace of organic structure could be detected. Analyses of material dried at 135° (I), and of undried material (II), gave the following results:—

	H_2O.	SiO_2.	Fe_2O_3.	Al_2O_3.	MgO.	Total.
I	3·59	88·87	5·26	1·84	0·32	99·88
II	8·87	84·36	4·99	1·74	0·30	100·26

The latter analysis corresponds with the composition of menilite, $H_2Si_3O_7$.

B. H. B.

Change in Colour in Felspar due to the Action of Light. By E. Erdmann (*Zeit. Kryst. Min.*, **10**, 493).—From the pegmatite veins of the Åmmeberg zinc mine, the author collected specimens of amazonite, with which he made the following experiments:—A large fragment was broken into three parts, 5 to 10 cm. long, the fresh fracture showing a pale greenish-grey colour. Of these pieces, one was packed up in black paper and kept in a dark place; the two others were exposed to the action of sunlight, one having a strip of black paper 10 mm. wide pasted on and varnished, the other having a strip of the same width varnished to exclude air and moisture, but not light. The two specimens were exposed to the action of the sun, air, and rain for 74 days. It was then found that the original pale

green colour had become a deep emerald-green; the portion protected by the black paper and the specimen kept in the dark room having remained unaltered. The layer of varnish had cracked, so that it could not be decided whether the change was due to air and moisture, or to light alone. A second experiment was then made. A piece of the unaltered felspar was broken up, and small pieces placed in five tubes of different colours (black, blue, yellow, pale emerald-green, and colourless). The open ends of the tubes were then sealed, without heating the felspar, and the tubes exposed to the action of light for 10 months. On opening the tubes, the felspar in the colourless tube was found to be of a deep emerald-green colour; the felspar in the green tube was less altered, still less in the yellow, and inappreciably in the blue, whilst in the black tube it was quite unaltered. The change in colour is due, therefore, to the action of light alone. B. H. B.

Apophyllite from Wermland. By L. J. IGELSTRÖM (*Zeit. Kryst. Min.*, **10**, 517).—At the Nordmarks mines the author found, in addition to the ordinary apophyllite in crystals, concentrically radiated globular masses of the same mineral, 2 to 3 cm. in diameter. An incomplete analysis gave the following results:—

SiO_2.	CaO.	MgO.	K_2O,Na_2O,F.	H_2O.	Total.
52·00	23·20	1·30	7·10	16·40	100·00

B. H. B.

Chemical Composition of the Amphiboles. By F. BERWERTH (*Zeit. Kryst. Min.*, **10**, 406—409).—1. *Tremolite.*—The mean of two analyses of tremolite from St. Gotthard gave the following results:—

SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	H_2O.	Total.	Sp. gr.
58·40	0·56	0·26	13·63	24·82	1·85	99·52	3·02

Making allowance for the talc mixed with the specimen analysed, the analysis corresponds with the formula

$$(CaSiO_3)(MgSiO_3)(H_2SiO_3).$$

2. *Actinolite.*—The author gives the formula for pure actinolite as

$$\left.\begin{matrix}5CaSiO_3\\9MgSiO_3\\2H_2SiO_3\end{matrix}\right\}$$

3. *Arfvedsonite*, from the Nunasornausak Mine in Greenland, gave on analysis the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	K_2O.	Na_2O.	H_2O.	Total.	Sp. gr.
47·08	1·44	1·70	35·65	2·32	2·88	7·14	2·08	100·29	3·45

The author assumes that muscovite is mixed with the mineral analysed, and that the formula for pure arfvedsonite is

$$\left.\begin{matrix}13FeSiO_3\\CaSiO_3\\4Na_2SiO_3\\2H_2SiO_3\end{matrix}\right\}$$

4. *Alumina-hornblende*, from Vesuvius, gave the following analytical results :—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.
39·80	14·28	2·56	19·02	10·73	9·10	2·85

Na_2O.	H_2O.	Total.	Sp. gr.
1·79	1·42	101·55	3·29

The author is of opinion that, as the amount of mica mixed with the hornblende is very small, the hornblende crystals were built up of calcium silicate and meroxene molecules, and assumes that at first the tendency to form meroxene predominated, but that the regular development of the meroxene was disturbed by the calcium silicate coming into play. By the calcium silicate and meroxene crystallising together, a hornblende crystal resulted as terminal product.

5. *Alumina-hornblende* (*Pargasite*), from the granular limestone of Pargas, had the following composition :—

F.	SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	K_2O.
1·66	42·97	16·42	1·32	14·99	20·14	2·85

Na_2O.	H_2O.	Total.	Sp. gr.
1·53	0·87	102·75	3·11

Subtracting the 35·91 per cent. of mechanically mixed phlogopite, the formula for the pure pargasite is

$$\left.\begin{matrix} 8Si_3Al_4O_{12} \\ 9SiCa_2O_4 \\ 7SiMg_2O_4 \\ SiH_4O_4 \end{matrix}\right\}$$

6. *Glaucophane*, from Zermatt, gave the following results on analysis :—

SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	Na_2O.	H_2O.	Total.	Sp. gr.
58·76	12·99	5·84	2·10	14·01	6·45	2·54	102·69	3·04

The quantity of paragonite admixed could not be determined.

B. H. B.

Alterations of the Garnets in the Amphibole Schists of the Tyrol. By A. Cathrein (*Zeit. Kryst. Min.*, **10**, 433—446).—In rocks from the Stamser Alps, the author has observed garnets altered into scapolite, epidote, oligoclase, hornblende, saussurite, and chlorite.

B. H. B.

Vesuvian Humite, Chondrodite from Nyakopparberg, and Humite from Ladugrufvan. By F. C. v. Wingard (*Zeit. Anal. Chem.*, **24**, 344—356).—The above minerals (with the exception of the Ladugrufvan humite) showed no trace of alteration to serpentine. The fluorine was determined by the direct method of Fresenius, except in the case of the Vesuvian humite of type II, and that from Ladugrufvan, where the small quantity of material would only allow of the

use of Berzelius' process. After drying at 110°, the minerals still contained hydrogen. This was determined by igniting with lead oxide and weighing the expelled water. The following are the analytical results:—

I. Vesuvian humite, type I, or humite of Descloiseaux.
II. Vesuvian humite, type II, or chondrodite of Descloiseaux. Pale wine-yellow.
III. Vesuvian humite, type III, or clinohumite of Descloiseaux. Pale brownish-yellow or greyish-brown.
IV. Chondrodite from Nyakopparberg: *a*, pale wine-yellow; *b*, honey-yellow.
V. Humite, type I, from Ladugrufvan.

	SiO_2.	MgO.	FeO.	Fe_2O_3.	MgF_2.	H_2O.	Total.
I	35·49	49·47	4·32	—	9·20	1·45	99·93
II	33·49	52·87	3·80	—	8·39	1·37	99·92
III	33·40	45·65	9·63	0·82	9·25	1·41	100·16
IV ... *a*.	33·90	47·65	7·76	0·11	9·10	1·31	99·83
IV ... *b*.	31·56	37·54	18·67	2·01	9·10	1·31	100·19
V	35·26	50·51	3·51	—	7·70	3·07	100·05

The completely unaltered condition of the specimens, and the fact that the water was not expelled below a red heat, negative the supposition of v. Rath that the deficiency in the older analyses was due to water of hydration, and require the hydrogen to be regarded as existing in the form of hydroxyl, replacing fluorine isomorphously. The fluorine determinations (of which the above numbers are the averages deduced from numerous concordant results) do not exhibit the wide variations found by other analysts, and, in fact, with the exception of II, in which it is assumed that the fluorine is below the truth, of IV*b*, which is rejected, and of the excess of water in V, due to an obvious partial alteration, all these numbers (after calculating the iron as magnesium) lead to the identical formula

$$Mg_{13}(MgF)_4(MgOH)_2(SiO_4)_8$$

for all the three types. M. J. S.

Isomorphous Silicates. By C. Rammelsberg (*Chem. Centr.*, 1885, 687—688).—The author has endeavoured, by a series of experiments, to add to the knowledge of the chemical nature of the members of the scapolite group. All the members of this group are perfectly isomorphous. They are called by various names, but qualitatively their composition is the same; they are silicates of alumina, lime, and soda. Only in one member, humboldtilite, do iron and magnesia occur to a considerable extent. There is no soda-free scapolite known, corresponding with anorthite, nor a lime-free scapolite, corresponding with albite, which, like the above-mentioned minerals of the felspar group, could be regarded as terminal members of the series. The composition of the various members of the group, however, is very different; the proportion of acid amounts to 40 to 60 per cent., that of lime varies from 24 to 4, whilst the amount of

soda amounts to 2 to 10 per cent. With the variations in the atomic proportion of Na : Ca : Al : Si, it appears desirable to assume Ca = 2R, Al = 6R, and to calculate the ratio R : Si. In this way the author found that the scapolite group includes: (A) semisilicates; (B) combinations of normal and semi-silicates; (C) normal silicates; and (D) combinations of normal and quadri-silicates. He concludes that in the scapolite group only the simplest silicates occur, namely:—

Normal.....	Na_2SiO_3; $CaSiO_3$; $AlSi_3O_9$.
Semisilicates	Na_4SiO_4; Ca_2SiO_4; $Al_2Si_3O_{12}$.
Quadrisilicates ...	$Na_2Si_2O_5$; $CaSi_2O_5$; $AlSi_6O_{15}$,

and combinations of any two of them. In group B, which includes the majority of cases, combinations of 1 and 6 mols., of 1 and 3 mols., of 1 and 1 mol., and of 4 and 1 mol. of normal and semi-silicate, are found. The combination of normal and quadri-silicate (group D) consists of 3 and 1 mol. B. H. B.

Mineralogical Notes from Bohemia. By R. Raffelt (*Zeit. Kryst. Min.*, **10**, 421).—In fissures and cavities in the basalt of the Eulenberg near Leitmeritz, the author found analcime, chabasite, phillipsite, and thomsonite, with aragonite and calcite. The analcime forms thin, crystalline crusts exhibiting the form 202. Chabasite occurs in yellow, twin crystals; phillipsite also occurs in twin crystals. On the latter are frequently planted crystals of thomsonite, with the following composition:—

SiO_2.	Al_2O_3.	CaO.	Na_2O.	H_2O.	Total.
38·44	31·48	13·60	3·53	12·93	99·98

B. H. B.

Empholite, a New Mineral from Horrsjöberg in Wermland. By L. J. Igelström (*Zeit. Kryst. Min.*, **10**, 521).—This new mineral forms white or yellowish, translucent crystals, and radiated aggregates in damourite and pyrophyllite in gneiss. The mineral crystallises in the rhombic system with the planes ∞P, ∞P̆∞, ∞P̆2, and ∞P̆3. The plane of the optic axes is parallel to the brachypinacoid; the acute bisectrix is parallel to the brachydiagonal, positive; the obtuse bisectrix is parallel to the vertical axis. In appearance the mineral resembles diaspore; H. = 6. Analysis gave the following results:—

SiO_2.	Al_2O_3.	MgO,CaO,FeO.	H_2O.	Total.
51·70	31·52	4·60	12·18	100·00

(Compare Abstr., 1885, 31.) B. H. B.

Persbergite. By L. J. Igelström (*Zeit. Kryst. Min.*, **10**, 522).—An analysis of the mineral discovered by the author in 1860, and named persbergite, shows it to be a mineral resembling falunite. The analytical results were as follows:—

SiO_2.	$Al_2O_3(Fe_2O_3)$.	MgO,CaO.	H_2O.	Total.
41·20	27·50	18·20	13·08	100·00

B. H. B.

Minerals from the Mica Diorite of Christianberg, Bohemia. By G. Starkl (*Zeit. Kryst. Min.*, **10**, 427).—The minerals examined were biotite, hornblende, plagioclase, and apatite. The three first minerals on analysis gave the following results :—

	SiO_2.	Al_2O_3.	Fe_2O_3.	Cr_2O_3.	FeO.	CaO.	MgO.	K_2O.
I..	39·53	13·45	8·06	0·14	4·89	3·38	22·52	4·13
II..	53·83	3·78	3·50	0·08	6·83	10·32	19·49	—
III..	65·54	21·74	trace	—	—	2·14	trace	3·32

	Na_2O.	H_2O.	Sp. gr.
I	1·22	1·49	2·81
II	—	1·04	2·92
III	7·75	0·35	2·57

Corresponding with the formulæ—

I. Biotite..... $2[(H_2Na_2K_2)_2SiO_4] + 11[(FeCaMg)_2SiO_4] + 3[(Al_2Fe_2Cr_2)_2Si_3O_{12}]$.

II. Hornblende . $15(RSiO_3) + 1(R_2'''Si_3O_9)$.

III. Plagioclase.. $2(K_2Al_2Si_6O_{16}) + 6(Na_2Al_2Si_6O_{16}) + 1(Ca_2Al_4Si_4O_{16})$.

B. H. B.

Chemical Constitution of Staurolite. By W. Friedl (*Zeit. Kryst. Min.*, **10**, 366—373).—Analyses of staurolite (I) from St. Gotthard and (II) from Tramnitzberg, in Moravia, gave the following results :—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	H_2O.	Total.
I ..	28·15	52·17	1·70	13·84	2·54	1·63	100·03
II ..	28·19	52·15	1·59	14·12	2·42	1·59	100·06

Both of these analyses correspond with the formula

$H_4(FeMg)_6(AlFe)_{24}Si_{11}O_{66}$, or $(FeMg)_6Al_6(AlO)_{18}(OH)_4(SiO_4)_{11}$.

This formula, based on analyses of material proved to be pure by microscopical examination, differs from Rammelsberg's formula for staurolite by $\frac{1}{2}$ mol. SiO_2. And the ferric oxide, passed over by Rammelsberg, is taken into account in the new formula. An estimate of the value of the two formulæ may be formed from the following comparison of the actual and calculated results :—

I. New staurolite formula, $H_4(Al,\frac{1}{48}Fe)_{24}(\frac{1}{3}Fe,Mg)_6Si_{11}O_{66}$.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	H_2O.	Total.
Calculated ..	28·38	51·87	1·68	13·93	2·58	1·55	99·99
Found	28·17	52·17	1·65	13·98	2·48	1·61	100·06

II. Old staurolite formula (according to Rammelsberg, taking into account the percentage of ferric oxide discovered by the author), $H_2(\frac{1}{3}Fe,Mg)_3(Al,\frac{1}{48}Fe)_{12}Si_6O_{34}$.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	H_2O.	Total.
Calculated..	30·18	50·58	1·64	13 58	2·51	1·51	100·00
Found.....	29·46	52·29	—	13·42	2·29	1·60	99·06

The percentage of alumina found by Rammelsberg exceeds the calculated amount by 1·71, whilst the silica percentage is 0·72 less than the calculated.

On comparing his analysis with that of the microscopically tested material, it is evident the staurolite he employed contained some quartz.

It may consequently be assumed that staurolite has the formula of a basic silicate :—

$$(MgFe)_6Al_6(AlO)_{18}(OH)_4(SiO_4)_{11} = H_4(Mg,Fe)_6(AlFe)_{24}Si_{11}O_{66},$$

which represents the simple oxygen ratio of 2 : 1. B. H. B.

Pycnophyllite from Aspang. By G. Starkl (*Zeit. Kryst. Min.*, **10**, 427—428).—The author gives the name of pycnophyllite to a compact, finely laminated substance, which fills the fissures of a talc-mica schist, south-east of Aspang. The mineral is of a green colour, is greasy to the touch, adheres to the tongue, has a resinous lustre, H. = 2, sp. gr. 2·796, is easily split up parallel to one plane. Thin leaves are translucent, biaxial, negative. In composition the mineral most resembles hygrophilite or pinite. The analyses of specimens from two localities in the neighbourhood of Aspang gave the following results :—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.
48·88	29·37	2·38	0·51	1·24	2·67	6·51	3·34	4·62
50·09	26·47	3·66	—	0·44	3·93	10·77		4·61

B. H. B.

Igelströmite from Delarne. By M. Weibull (*Zeit. Kryst. Min.*, **10**, 511).—This mineral, formerly described by the author (Abstr., 1884, 409), from the Silferberg mines, has been recently found four miles further to the south-west in the Hillängs mines. The deposit consists of magnetite with manganocalcite, silicates rich in manganese (igelströmite, actinolite, and garnet), arsenical pyrites, and magnetic pyrites. An analysis of the igelströmite gave the following results :—

SiO_2.	FeO.	MnO.	MgO.	$CaCO_3$.	Total.
28·76	48·59	18·57	1·98	2·25	100·15

corresponding with the formula—

$$2(FeMg)_2SiO_4 + (MnMg)_2SiO_4.$$

B. H. B.

Minerals of Vester-Silfberg. By M. Weibull (*Zeit. Kryst. Min*, **10**, 512—515).—The author gives a detailed description of a number of minerals occurring at Vester-Silfberg. Manganocalcite from the Stollberg gave on analysis the following results :—

CaO.	MnO.	FeO.	MgO.	CO_2.	Insoluble.	Sp. gr.
46·22	6·98	3·01	0·22	(42·86)	0·71	2·804

corresponding with the formula $6CaCO_3 + (MnFe)CO_3$. The mineral

thus approximates closely to Breithaupt's so-called spartaite. An analysis of manganese-hisingerite, an alteration-product of igelströmite, gave the following results :—

SiO_2.	Fe_2O_3.	Mn_2O_3.	Al_2O_3.	MgO.	CaO.	H_2O.	Total.	Sp. gr.
37·09	34·34	15·50	1·39	2·62	1·92	7·81	100·67	2·469

An analysis of silfbergite gave—

SiO_2.	FeO.	MnO.	MgO.	CaO.	Al_2O_3.	Ignition.	Total.
49·50	30·69	8·24	8·10	2·02	0·69	0·40	99·64

corresponding with the formula $(FeMnMgCa)SiO_3$.

The author further mentions the occurrence of magnetite, igelströmite, iron-rhodonite, and manganese-hedenbergite (compare Abstr., 1884, 409). B. H. B.

Manganese Minerals from Wermland. By L. J. IGELSTRÖM (*Zeit. Kryst. Min.*, **10**, 519—521).—The manganese minerals of the so-called steel ore mines of Gåsborn in Wermland, are manganese silicates, and are largely employed in steel making. The author has made several analyses of these silicates, the results being as follows:—

	SiO_2.	MnO.	FeO.	CaO.	MgO.	Al_2O_3.	Fe_2O_3.	Ignition.	Total.
I.	42·37	40·63	6·80	8·10	—	—	—	2·10	100·00
II.	47·00	31 20	10·60	5·70	2·50	—	—	0·80	97·81
III.	38·63	13·00	—	19·80	—	8·20	21·90	—	101·53

I. Rhodonite; II. Rhodonite, with grains of magnetite; III. brownish and manganese garnet.

A yellow manganese silicate gave the following analytical results :—

SiO_2.	FeO.	MnO.	CaO.	Total insoluble in acids.
38·35	14·05	29·52	10·52	92·46

$MnCO_3$.	$FeCO_3$.	$CaCO_3$.	Total soluble in acids.
3·70	2·01	1·36	7·07

B. H. B.

Chemical Composition of Kataplëite. By A. SJÖGREN (*Zeit. Kryst. Min.*, **10**, 509—510).—The mean of two new analyses of kataplëite is as follows:—

SiO_2.	ZrO_2.	FeO.	CaO.	Na_2O.	H_2O.	Total.
44·13	32·00	0·19	5·56	8·52	9·26	99·66

The author, therefore, concludes that the formula of kataplëite is $(Na_2CaFe)SiO_3 + ZrSi_2O_6 + 2H_2O$. B. H. B.

Two New Norwegian Minerals. By W. C. BRÖGGER (*Zeit. Kryst. Min.*, **10**, 503—504).—1. *Lavenite.* Monosymmetrical. Axial ratio $a:b:c = 1·0811:1:0·8133$; $\beta = 71° 24\frac{1}{2}'$, with the combination

∞P, $\infty P2$, $\infty P\infty$, $\infty P\infty$, $-P$, $-P\infty$. The optic axial plane is the plane of symmetry, the acute bisectrix forming with the vertical axis an angle of $20\frac{1}{2}°$. Cleavage perfect in the direction of the orthopinacoid. Colour chesnut-brown to yellow. Slightly translucent. Analysis gave the following results :—

SiO_2.	ZrO_2.	Fe_2O_3.	MnO.	CaO.	Na_2O.	Ignition.	Total.	Sp. gr.
33·71	31·65	5·64	5·06	11·00	11·32	1·03	99·41	3·51

This very rare mineral was formerly regarded by the author as mosandrite, which it closely resembles.

2. *Cappelenite.*—A greenish-brown mineral in thick prismatic crystals, translucent to semi-transparent. Hexagonal; axial ratio $a : c = 1 : 0{\cdot}43010$; combination, ∞P, P, 3P, 0P.

Analysis gave the following results :—

SiO_2.	B_2O_3.	Y_2O_3.	$(LaDi)_2O_3$.	Ce_2O_3.	ThO_2.	BaO.
14·16	(17·13)	52·55	2·97	1·23	0·79	8·15

CaO.	Na_2O.	K_2O.	H_2O.	Total.	Sp. gr.
0·61	0·39	0·21	1·81	100·00	4·407

B. H. B.

Barium Sulphate as a Cementing Material in Sandstone. By F. Clowes (*Chem. News*, **52**, 194).—In certain New Red Sandstone beds in the neighbourhood of Nottingham, known as Stapleford and Bramcote Hills, and the Hemlock Stone, the cementing material has been shown by the author to be crystalline barium sulphate. The Hemlock Stone is mushroom shaped, and whilst the lower portion is calcareous sandstone, the upper portion is not, but contains barium sulphate, to which fact most probably the stone owes its shape. The barium sulphate occurs in some of the beds in streaks, patches, and large and small more or less spherical masses; the intervening sand being loose, weathered surfaces appear honey-combed or mammellated, and in one case yield pebble-like masses of sand held together by barium sulphate. D. A. L.

Weathering of Sandstone. By J. Stoklasa (*Landw. Versuchs-Stat.*, 1885, 203—214).—The sandstone examined contained 41 per cent. of quartz, and had a sp. gr. of 2·3—2·5 at 17°. The changes which this class of stone undergoes may be thus classified: oxidation of the ferrous compounds (yellowing); partial solution of carbonates; loss of half the total calcium carbonate with relative increase of silicates and quartz; and final pulverisation of the mass. The analytical tables show clearly the conversion of insoluble into soluble compounds, especially in the case of the phosphates which rapidly become soluble in acetic and citric acids. E. W. P.

Application of Thermochemistry to Geology. By Dieulafait (*Compt. rend.*, **101**, 609—612, 644—646, and 676—679).—The object of the author's investigations is to ascertain how far the main facts of geology can be explained by thermochemical laws, the inquiry being

limited in the present papers to the formation of minerals at the ordinary temperatures from substances in aqueous solution.

From a consideration of the following reactions—

$2FeO + O = Fe_2O_3$,	develops	+ 26·6 cal.
$2MnO + O_2 = 2MnO_2$,	„	+ 21·4 „
$2FeO + 2CO_2 = 2FeCO_3$,	„	+ 10 0 „
$2MnO + 2CO_2 = 2MnCO_3$,	„	+ 13·6 „

it would follow that when oxygen and carbonic anhydride, *both in excess*, come in contact with silicates or other minerals containing ferrous and manganous oxides, the latter will be converted into ferric oxide and manganese peroxide respectively, and no carbonates will be formed. If, however, the carbonic anhydride and oxygen come in contact with the minerals slowly and in quantity insufficient to completely transform both oxides, the oxygen will combine mainly, if not entirely, with the ferrous oxide, and the carbonic anhydride, being unable to combine with the ferric oxide thus formed, will unite with the manganous oxide in preference to uniting with the still unaltered ferrous oxide. The products will, therefore, be ferric oxide, which is insoluble, and manganous carbonate, which is distinctly soluble. If the two gases are dissolved in water percolating through primary rocks, the issuing water will contain manganous carbonate in relatively much greater proportion than in the original rock, and it is easy to see that this explains the formation of manganese minerals comparatively free from iron, from rocks in which iron is present in considerable quantity.

Since the heat of formation of ferric oxide is so much greater than that of ferrous carbonate, it follows that the latter can only be formed in a reducing medium, and can only remain unchanged so long as it is protected from the action of oxygen. Natural ferrous carbonates may be divided into two groups: spathic iron, which is crystallised, and exists in the oldest rocks as well as in comparatively recent formations; and lithoidal ferrous carbonate, which is confined to the carboniferous horizon. The formations in which this lithoidal ferrous carbonate occurs, are of estuarine origin, and hence the ferrous carbonate has been formed in a reducing medium highly charged with carbonic anhydride.

The iron in alluvial formations is invariably present as hydrated ferric oxide, which is generally supposed to have been brought up by the water springing from the underlying rocks. If this explanation were correct, we should expect to find crystallised ferrous carbonate deposited in the caverns and fissures in these rocks, but as a matter of fact, the whole of the iron which they contain is in the state of hydrated peroxide. This would indicate that the iron has really been derived from water percolating from above.

Amongst the natural compounds of a metal, that with the greatest heat of formation should constitute the principal mineral of the particular metal. If all minerals had been deposited from aqueous solutions of tolerably simple composition, it would follow from the laws of thermochemistry that there should only be one naturally occurring compound of each metal, but many minerals have been

formed in very complex media and under extremely varied conditions, and these geological conditions have to be taken into account. All minerals may, however, be broadly divided into the following types: those which have been formed in an oxidising medium; those which have been formed in a reducing medium; those which have been deposited on a siliceous substratum; and those which have been deposited on a calcareous substratum.

The heats of formation of the more important manganese compounds are manganous sulphide, MnS, 22·6 cal.; manganous oxide, MnO, 47·4 cal.; manganous carbonate, $MnCO_3$, 54·2 cal.; and manganese peroxide, MnO_2, 58·1 cal. These values are in complete agreement with the fact that manganese peroxide is by far the most abundant mineral of manganese, that manganous sulphide is very rare, whilst manganous oxide exists only in combination with the peroxide, and that manganous carbonate is a rare mineral, mainly confined to veins and fissures, and existing only out of contact with oxygen. In all cases where the oxidation of the manganese is not complete this result is due to the non-permeable character of the minerals by which the manganese compound is surrounded.

C. H. B.

Composition of Water from Uriage (Isère). By E. Peligot (*J. Pharm.* [5], **11**, 241—245).—Berthier examined this water in 1823, and found the solid residue to be 5·76 grams per litre; twenty years later this became almost doubled in amount, and has since remained constant. The following is the result of the author's analysis:—

$CaCO_3$.	NaCl.	KCl.	$CaSO_4$.	Na_2SO_4.	$MgSO_4$.	Na_2HAsO_4.
0·388	6·000	0·402	1·143	1·253	0·609	0 002

SiO_2.	H_2S.	Total.
0·014	0·010	9·821

The total solid residue was 11·917 grams, the excess being due to water of crystallisation of the sulphates. The presence of minute traces of iodine and boric acid was ascertained, the latter having been previously found by Dieulafait. Lefort has detected lithium, rubidium, ferrous sulphide, sodium thiosulphate, and organic matter. Sp. gr. 1·0084; dissolved gases, nitrogen 19 c.c., carbonic anhydride, 3·2 c.c., at 0° and 760 mm. The other constituents agree closely with those obtained by the author. The probable origin of the water is discussed. The water is accompanied by enormous quantities of gas, which is mainly composed of nitrogen and carbonic anhydride.

J. T.

Organic Chemistry.

Melting and Boiling Points of Cyanogen Bromide. By E. MULDER (*Rec. Trav. Chim.*, **4**, 151—152).—Cyanogen bromide becomes somewhat transparent at 16°, but melts at about 52°, it boils at 61·3° (corr.). A. P.

Normal Cyanuric Acid. By E. MULDER (*Rec. Trav. Chim.*, **4**, 91—101).—In continuation of his researches on the derivatives of normal cyanic acid (Abstr., 1883, 304, and *Rec. Trav. Chim.*, **2**, 133) the author finds that both normal ethyl cyanurate and the crude product $x(CN{\cdot}OEt{\cdot}C_2H_6O)$ (Abstr., *loc. cit.*), when saponified with aqueous soda at the ordinary temperature, and then neutralised with hydrochloric acid, yield a white crystalline deposit having the composition $C_3N_3O_3HEt_2$, and probably the constitution $C_3N_3(OEt)_2{\cdot}OH$ or $C_2N_2(OEt)_2{\cdot}CONH$. Normal ethyl cyanurate yields isocyanuric acid on acidification with hydrochloric acid, normal cyanuric acid seeming to be incapable of existing in the free state. The author considers that Wurtz's diethylcyanuric acid is most probably identical with that obtained by Habich and Limpricht, and has the constitution $C_3O_3(NEt)_2{:}NH$. A. P.

Additive Compounds of Normal Ethyl Cyanurate with Cyanogen Bromide. By E. MULDER (*Rec. Trav. Chim.*, **4**, 147—150).—On treating normal ethyl cyanurate with excess of cyanogen bromide, an additive compound, $C_3N_3O_3Et_3,2CNBr$, is formed. It is liquid at the ordinary temperature, crystallising a few degrees lower. The author considers that it has the constitution

$$NC{\cdot}N<\begin{matrix}CBr(OEt){\cdot}N{:}C(OEt)\\ CBr(OEt)\text{——}N(CN)\end{matrix}>$$

When heated for several hours at 125°, until no further pressure is developed, a yellow liquid is formed, which by continued heating at the same temperature in an open tube is converted into a hard and vitreous mass.

On treating cyanogen bromide with excess of normal ethyl cyanurate, a second additive compound seems to be formed, having the composition $C_3N_3O_3Et_3,CNBr$. A. P.

Action of Ammonia and Amines on Methyl Thiocyanurate and Cyanuric Chloride. Normal Alkyl Melamines. By A. W. HOFMANN (*Ber.*, **18**, 2755—2781).—The final product of the action of ammonia on methyl thiocyanurate is *melamine*, but by modifying the conditions of the experiment, either of the intermediate products may be produced. To obtain the *primary amido-base*, $C_3N_3(SMe)_2{\cdot}NH_2$, the methyl thiocyanurate is digested with a moderate excess of strong *alcoholic* ammonia for about five hours at 100°. The purified base crystallises from boiling alcohol in rhombic plates melting at 200; it

is readily soluble in hot, more sparingly in cold alcohol, and is not quite insoluble in water. Its solutions give no reaction with vegetable colours, and no sulphur reaction with alkaline lead salts. The base dissolves sparingly in hydrochloric acid, and is reprecipitated on the addition of water. On boiling it for a long time with hydrochloric acid, it is decomposed with production of mercaptan, ammonia, and cyanuric acid. The platinochloride and aurochloride,

$$C_5H_8N_4S_2,HAuCl_4,$$

are described. The *secondary amido-base*, $C_3N_3(NH_2)_2{\cdot}SMe$, is obtained on digesting methyl thiocyanurate with *alcoholic* ammonia for about five hours at 160°. It differs from the primary base by its ready solubility in water and more sparing solubility in alcohol; it melts at 268°, dissolves readily in hydrochloric acid, and yields a platinochloride, $(C_4H_7N_5S)_2,H_2PtCl_6$. When boiled with hydrochloric acid, it gives the same decomposition-products as the monamido-compound. The *tertiary amido-base, melamine*, can be obtained in nearly theoretical amount by heating methyl thiocyanurate with an excess of strong aqueous ammonia for several hours at 180°. Its properties agree with those assigned to it by Liebig (*Annalen*, **10**, 21). The author has also succeeded in obtaining two platinochlorides from it,

$$(C_3H_6N_6)_2,H_2PtCl_6 + 2H_2O \text{ and } C_3H_6N_6,H_2PtCl_6 \text{ (?)}.$$

The amines are found to react with methyl thiocyanurate in the same way as ammonia. The *primary methylamido-base*, $C_3N_3(SMe)_2{\cdot}NHMe$, is produced on heating methyl thiocyanurate with a 33 per cent. aqueous solution of methylamine for several hours at 100°. It is readily soluble in alcohol and ether, and crystallises in well-formed prisms melting at 174—175°; it forms crystalline salts with hydrochloric, nitric, and oxalic acids, and also yields a sparingly soluble platinochloride and an aurochloride. Hydrochloric acid decomposes the base at 100° into ethyl mercaptan, methylamine, and cyanuric acid. The *secondary methylamido-base*, $C_3N_3(NHMe)_2{\cdot}SMe$, is produced simultaneously with the primary compound. It is very readily soluble in alcohol, less so in ether, and is best crystallised from a large bulk of boiling water, from which it separates in slender needles melting at 144°. Its salts are mostly very readily soluble, the nitrate crystallising best; the platinochloride is very sparingly, and the aurochloride moderately soluble. The base is decomposed by hydrochloric acid at 200°, and yields the same products as the primary base.

The *tertiary methylamido-base, trimethylmelamine*, is prepared by heating methyl thiocyanurate with 33 per cent. aqueous methylamine for several hours at 180°; or a mixture of the primary and secondary bases may first be prepared at a temperature of 130—140°, and this then heated at 170—180° with more methylamine. Trimethylmelamine is very readily soluble both in water and in alcohol, and the author has not succeeded in obtaining it quite pure; its hydrochloride, nitrate, and sulphate are also extremely soluble, the oxalate more sparingly so. Like melamine, it yields two platinochlorides,

$$[C_3N_3(NHMe)_3]_2,H_2PtCl_6 \text{ and } C_3N_3(NHMe)_3,H_2PtCl_6.$$

By the action of ammonia on cyanuric chloride, Liebig (*Annalen*, **10**, 45) obtained the compound $C_3H_4N_5Cl$, which he termed chlorocyanamide, but which the author shows to be $C_3N_3(NH_2)_2Cl$, that is an intermediate product between cyanuric chloride and melamine, and it may in fact be converted into the latter by a few hours' heating at 100° with strong aqueous ammonia. A nearly theoretical yield of melamine may likewise be obtained directly from cyanuric chloride. A solution of methylamine in absolute methyl alcohol likewise reacts with cyanuric chloride with production of *dimethylamidocyanuric chloride*, $C_3N_3(NHMe)_2Cl$; it is nearly insoluble in water, alcohol, and ether, soluble with slight decomposition in boiling glacial acetic acid, from which hot water precipitates it in needles melting at 241° with decomposition. In acid solutions, the chlorine soon becomes replaced by hydroxyl. When dimethylamidocyanuric chloride is heated with a solution of methylamine in methyl alcohol for a few hours at 100°, it is converted into trimethylamine; this, when heated at 150° with hydrochloric acid, splits up into methylamine and cyanuric acid. On heating dimethylamidocyanuric chloride with aqueous ammonia at 150°, the chlorine is displaced, and a base produced which is without doubt *dimethylmelamine*, $C_3N_3(NHMe)_2{\cdot}NH_2$; its salts are soluble, the sulphate crystallising in six-sided plates, and the oxalate in rhombic crystals; it yields two platinochlorides, $C_5H_{10}N_6,H_2PtCl_6$ and $(C_5H_{10}N_6)_2,H_2PtCl_6$.

The *dimethylamidocyanuric acid*, $C_3N_3(NHMe)_2{\cdot}OH$, obtained from dimethylamidocyanuric chloride (see above) by the action of an acid (or of water at 200°), is separated from its hydrochloride as a white indistinctly crystalline precipitate which is almost insoluble in boiling water, insoluble in alcohol and ether; its platinochloride has the formula $(C_5H_9N_5O)_2,H_2PtCl_6$. Dimethylamidocyanuric acid forms salts both with acids and with bases; the hydrochloride and nitrate are crystalline and soluble without decomposition; the sodium salt and the methyl salt (obtained from dimethylamidocyanuric chloride and sodium methylate) crystallise in prisms.

The mother-liquors from the preparation of dimethylamidocyanuric chloride contain (besides methylamine hydrochloride) a crystalline substance, found to be *methylamidomethoxycyanuric chloride*,

$$MeO{\cdot}C_3N_3Cl{\cdot}NHMe;$$

it forms acicular crystals melting at 155°, is soluble in alcohol and ether, also in hydrochloric and nitric acids with formation of crystallisable salts. It may be boiled with acids without parting with its chlorine.

Attempts to obtain *hexamethylmelamine*, $C_3N_3(NMe_2)_3$, by heating methyl thiocyanurate with dimethylamine, were without success, but its hydrochloride may be obtained by heating a mixture of equal weights of dimethylamine hydrochloride and cyanuric chloride as long as hydrogen chloride is evolved. The base crystallises in needles melting at 171—172°; its platinochloride and aurochloride are described. When it is heated with hydrochloric acid at 200°, it splits up into cyanuric acid and dimethylamine.

Methyl thiocyanurate is acted on by ethylamine in the same way as

by ammonia and by methylamine with formation of corresponding products. The *primary ethylamido-base*, $C_3N_3(SMe)_2{\cdot}NHEt$, crystallises from boiling dilute alcohol in lustrous needles melting at 114°, is sparingly soluble in boiling water, readily in cold alcohol; it yields a platinochloride of the formula $(C_7H_{12}N_4S_2)_2,H_2PtCl_6$. The *secondary ethylamido-base*, $C_3N_3(NHEt)_2{\cdot}SMe$, forms needles melting at 83—84°; its hydrochloride is crystalline, extremely soluble in water, less so in alcohol, and insoluble in ether; the nitrate is more sparingly soluble; the oxalate forms slender, very soluble needles, whilst the sulphate does not crystallise. A platinochloride, aurochloride, and stannochloride have also been obtained. The *tertiary ethylamido-base*, *triethylmelamine*, $C_3N_3(NHEt)_3$, can be obtained both from methyl thiocyanurate and from cyanuric chloride, and forms prisms melting at 73—74°. It is soluble in alcohol, ether, and benzene; the platinochloride, $(C_9H_{18}N_6)_2,H_2PtCl_6$, and aurochloride are described, and also a compound with silver nitrate, $(C_9H_{18}N_6)_2,AgNO_3$. Triethylmelamine is decomposed by hydrochloric acid at 150° into cyanuric acid and ethylamine.

Hexethylmelamine, $C_3N_3(NEt_2)_3$, is formed by the action of diethylamine on cyanuric chloride. The platinochloride, $(C_{15}H_{30}N_6)_2,H_2PtCl_6$, and aurochloride, $C_{15}H_{30}N_6,HAuCl_4$, are described. Hydrochloric acid at 150° decomposes the base into diethylamine and cyanuric acid.

In order to show that the higher amines also react with methyl thiocyanurate, this latter substance was digested with alcoholic amylamine at 100°. The *primary amylamido-base*, $C_3N_3(SMe)_2{\cdot}NHC_5H_{11}$, obtained, crystallises in clusters of silky needles melting at 96°. Hydrochloric acid decomposes it slowly at the ordinary temperature.

Piperidine also reacts with methyl thiocyanurate. When the reaction takes place at 200°, the *secondary base*, $C_3N_3(NC_5H_{10})_2{\cdot}SMe$, is obtained, and forms colourless crystals melting at 106—107°; its platinochloride has the formula $(C_{11}H_{23}N_5S)_2,H_2PtCl_6$. If the reaction takes place at 250°, the *tertiary base*, *tripiperidylmelamine*,

$$C_3N_3(NC_5H_{10})_3,$$

is produced, and crystallises in small needles melting at 213°; it dissolves readily in acids, and yields a sparingly soluble platinochloride, $(C_{18}H_{30}N_6)_2,H_2PtCl_6$. Hydrochloric acid decomposes the base at 150° into piperidine and cyanuric acid.

Triphenylmelamine, $C_3N_3(NHPh)_3$, may be obtained by the action of aniline on methylthiocyanurate or cyanuric chloride, and *hexaphenylmelamine*, $C_3N_3(NPh_2)_3$, may likewise be obtained from diphenylamine and cyanuric chloride. A. K. M.

Alkyl Isomelamines derived from the Alkyl Cyanamides, and the Constitution of Melamine and of Cyanuric Acid. By A. W. Hofmann (*Ber.*, **18**, 2781—2800).—Of the two formulæ, $NH_2{\cdot}C\lessdot^{N{\cdot}C(NH_2)}_{N:C(NH_2)}\gtrdot N$ and $NH:C\lessdot^{NH{\cdot}C(NH)}_{NH{\cdot}C(NH)}\gtrdot NH$, which have been proposed for melamine, the former is the one which most simply explains the formation of melamines and of mercaptan by the action of ammonia or amines on methyl thiocyanurate, and of melamines and

hydrochloric acid from cyanuric chloride and ammonia or amines (see last Abstract). The second formula, on the other hand, would necessitate the assumption of complicated molecular changes; in the formation of the hexalkylmelamines by the action of a secondary amine, one alkyl group of the latter must be assumed to detach itself from one nitrogen-atom, and to attach itself to another, and the resulting hexalkylmelamine, $NMe:C<^{NMe\cdot C(NMe)}_{NMe\cdot C(NMe)}>NMe$, should be split up by the action of water into methyl cyanurate and methylamine; cyanuric acid and dimethylamine are, however, produced. The formation of the piperidine-derivative of melamine is met by similar difficulties if the imido-formula be taken as correct, whilst the amido-formula readily explains all the reactions.

Alkylmelamines corresponding with an *imido-melamine* can, however, be obtained, but these yield no cyanuric acid; they split up into ammonia and alkyl cyanurates.

Trimethylisomelamine, $C_3N_3Me_3(NH)_3$, has been previously mentioned by the author (*Ber.*, **3**, 264) and by Baumann (*Ber.*, **6**, 1372). In order to obtain it, monomethylthiocarbamide is treated with dry mercuric oxide in absolute alcohol, the methylcyanamide first formed rapidly polymerising to trimethylisomelamine. This is very readily soluble in water and alcohol, insoluble in ether, the solution exhibiting a distinctly alkaline reaction. It crystallises in well-formed needles, melts at 179° and readily sublimes; the platinochloride, $C_6N_6H_{12},H_2PtCl_6$, and aurochloride, $C_6N_6H_{12},H_2Au_2Cl_8$, are described. Hydrochloric acid at 100° decomposes the base into *ammonia* and *methyl isocyanurate;* this decomposition takes place in stages, and the author has succeeded in isolating one of the two intermediate products, namely, $NH:C_3N_3Me_3O_2$; it forms an aurochloride,

$$C_6H_{10}N_4O_2,HAuCl_4,$$

and a hydrochloride, $C_6H_{10}N_4O_2,HCl$.

Triethylisomelamine, $C_3N_3Et_3(NH)_3$, has also been previously mentioned (Hofmann, *Ber.*, **1**, 27). It forms stellate groups of needles, melts at 92°, and crystallises from water with 4 mols. H_2O. Platino- and auro-chlorides are described. It is decomposed by acids in the same way as the trimethyl-derivative, and here again the one intermediate product, $HN:C_3N_3Et_3O_2$, can readily be isolated.

In further support of the amido-nature of melamine, the author mentions its decomposition by water into ammonia and cyanuric acid, the constitution of which he indicates to be $HO\cdot C<^{N\cdot C(OH)}_{N:C(OH)}>N$. He points out that the formation of cyanuric acid from carbamide does not prove it to have the constitution $CO<^{NH\cdot CO}_{NH\cdot CO}>NH$, as the constitution of carbamide has not been definitely established (compare this Journal, 1866, 161). There also appears to be little ground for the assumption of the iso-nature of cyanic acid. On the contrary, the formation of cyanates from potassium cyanide, the conversion of ammonium cyanate into carbamide, and of cyanic acid with the elements of water into ammonia and carbonic anhydride, run perfectly

parallel with the formation and behaviour of thiocyanic acid, the normal constitution of which is not doubted. The formation of alkyl isocyanurates from cyanuric acid may be accounted for by the fact that the normal ethers may be readily converted into the iso-ethers (*Ber.*, **3**, 272; *Rec. Trav. Chim.*, **1**, 191). The production of cyanuric chloride from phosphorus pentachloride and cyanuric acid, and the re-formation of the latter by the action of water on the chloride (*Annalen*, **116**, 357) also support the view that cyanuric acid contains hydroxyl-groups. Phosphorus pentachloride acts in the same way on the normal methyl salt of cyanuric acid, with formation of methyl chloride, phosphorus oxytrichloride, and cyanuric chloride. Methyl isocyanurate, however, gives a very different reaction when heated with phosphorus pentachloride, hydrochloric acid, phosphorus trichloride, and trichloromethyl isocyanurate,

$$\cdot CO<\begin{matrix}N(CH_2Cl)\cdot CO\\N(CH_2Cl)\cdot CO\end{matrix}>N(CH_2Cl),$$

being formed. A. K. M.

Allyl-sulphuric Acid. By F. Szymanski (*Annalen*, **230**, 43—50).—The preparation of allyl-sulphuric acid by the action of sulphuric acid on allyl alcohol was first described by Cahours and Hofmann (*Annalen*, **102**, 293). Beilstein and Wiegand (Abstr., 1885, 740) have recently stated that allyl alcohol is completely carbonised by sulphuric acid. The author finds that this is not the case when the alcohol is slowly added to the acid. The best results are obtained when the acid is diluted with an equal volume of water. The barium salt has been previously described by Cahours and Hofmann (*loc. cit.*). The *strontium* salt forms anhydrous, rhombic prisms soluble in water and in alcohol. The anhydrous *calcium* salt crystallises in quadratic plates. The copper salt crystallises in needles with 4 mols. H_2O. It is soluble in water and alcohol. On saturating allyl-sulphuric acid with lead carbonate, a basic salt, $(C_3H_5SO_4)_2Pb + PbO + 6H_2O$, is obtained, which is soluble in water.

The *magnesium salt*, $Mg(C_3H_5SO_4)_2 + 4H_2O$, crystallises in transparent needles, soluble in water. The *potassium*, *ammonium*, and *sodium* salts are hygroscopic and soluble in water. The *ferrous* salt forms quadratic plates soluble in alcohol. It is hygroscopic.

W. C. W.

Methylene-derivatives. By L. Henry (*Compt. rend.*, **101**, 599—600).—*Diethoxymethane*, $CH_2(OEt)_2$, obtained by the action of diiodomethane on sodium ethoxide, is a colourless, mobile, limpid liquid, with a pungent taste, and a peculiar agreeable odour quite different from that of acetal. It is only slightly soluble in water, and quite insoluble in a concentrated solution of calcium chloride. It boils at 82—83° under a pressure of 760 mm.; sp. gr. at 16·7° compared with the water at the same temperature = 0·8275; vapour-density 3·44.

Chlorobromomethane, CH_2ClBr, obtained by the action of excess of bromine on chloriodomethane, is a mobile, colourless liquid with an agreeable ethereal odour and a sweetish, pungent taste. It is insoluble in water, does not decompose when exposed to light, and boils at

68—69° under a pressure of 765 mm.; sp. gr. at 19° compared with water at the same temperature = 1·9907; vapour-density 4·43.

Bromiodomethane, CH_2BrI, is obtained by the action of a limited quantity of bromine, or better, of iodine chloride, on diiodomethane. It is a colourless liquid which becomes purple when exposed to light. It has an agreeable ethereal odour and a sweetish, bitter taste, is insoluble in water, and boils at 138—140° under a pressure of 754 mm.; sp. gr. at 16·8° compared with water at the same temperature = 2·9262; vapour-density 7·65. C. H. B.

Sulphates of some Carbohydrates. By M. Hönig and S. Schubert (*Monatsh. Chem.*, **6**, 708—749).—By the action of sulphuric acid on cellulose at different temperatures, varying from 7° to 40°, and subsequent treatment of the product with barium carbonate, salts were obtained which contained the same percentage of barium, but which possessed a greatly varying rotatory power ($[\alpha]_j = -3·65°$ to $+72·99°$). Further experiments made to ascertain the influence of the quantity of acid used, showed that salts varying in composition, but having the same rotatory power, can be formed. Prolonged action of sulphuric acid causes an increase of barium in the salt as well as an increase of rotatory power. When the action is allowed to take place at a low temperature the product contains salts varying more from one another than if the reaction takes place at a higher temperature.

The following salts were separated:—

$$C_{18}H_{26}O_{11}(SO_4Ba)_4,\ C_{12}H_{17}O_7(SO_4Ba)_3,\ C_{42}H_{62}O_{27}(SO_4Ba)_8.$$

They form white or yellowish-white, voluminous powders, with varying solubilities in water; the *lead* and *calcium* salts are similar. The hydrogen sulphates form white, amorphous, very hygroscopic compounds, which dissolve very readily in water and in alcohol; they are insoluble in ether. The aqueous solution decomposes slowly at the ordinary temperature, more quickly when boiled, losing sulphuric acid.

Anhydrous starch is acted on by sulphuric acid in a similar way; but the action is much slower than in the case of cellulose. The products have the same general formula, $C_{6n}H_{10n}O_{5n-x}(SO_4)_x$, as those obtained from cellulose, but turn polarised light to the right.

When the hydrogen sulphates are boiled with alcohol, they lose all the sulphuric acid, leaving modified forms of cellulose and starch respectively. N. H. M.

Organic Iodides of Nitrogen. By F. Raschig (*Annalen*, **230**, 221—224).—Methylamine hydrochloride is completely converted into *methyldiiodamine*, NI_2Me, when the theoretical quantity of iodine (dissolved in potassium iodide) is added to a solution of methylamine hydrochloride and sodium hydroxide: $MeNH_2,HCl + 4I + 3NaOH = NMeI_2 + NaCl + 2NaI + 3H_2O$.

Dimethyliodamine, NMe_2I, is obtained from dimethylamine by a similar reaction as a yellow precipitate. It is sparingly soluble in alcohol and ether. It soon decomposes and acquires a dark colour. A solution of potash changes the colour of the compound to greenish-yellow without

affecting its composition. Iododimethylamine and di-iodomethylamine decompose without exploding when they are touched by a hot body.

Ethyldi-iodamine and *diethyliodamine* are obtained by similar reactions, in the form of brick-red and orange-coloured precipitates. They rapidly decompose into iodoform and a dark blue liquid.

W. C. W.

Synthesis of a Ketone from Œnanthylidine. By A. M. Béhal (*J. Pharm.* [5], **11**, 155—158).—*Amyl methyl ketone*, C_5H_{11}·COMe, is obtained by dissolving œnanthylidine in sulphuric acid, diluting with water and distilling. It forms an oily liquid of pungent odour, boils at 147—148° under 759·2 mm. pressure, shows the property of a ketone, yielding a hydrogen sodium sulphite compound, &c., and on oxidation is converted into acetic and valeric acids. A. J. G.

Action of Bromine in Alkaline Solution on Amides. By A. W. Hofmann (*Ber.*, **18**, 2734—2741).—Chloracetamide is acted on by bromine in alkaline solution with formation of a compound, $CH_2Cl·NH·CO·NH·C_2H_2ClO$. This substance melts at 180°, and is sparingly soluble; it is decomposed by acids or alkalis into chloracetic and hydrochloric acids, carbonic anhydride, ammonia, and methaldehyde. Ethoxyacetamide, when treated with an alkaline solution of bromine, yields a compound, $EtO·CH_2·NH·CO·NH·C_2H_2O·OEt$. It crystallises in colourless needles, which melt at 80°, and is decomposed by acids and alkalis into ethoxyacetic acid, alcohol, ammonia, and methaldehyde.

When 1 mol. of phenylacetamide is acted on by 1 mol. bromine and 4 mols. of a 5 per cent. solution of alkali, and then distilled in steam, much benzylamine is obtained together with some bromobenzylamine, which may be converted by the action of sodium amalgam into benzylamine. The yield is about 60 per cent. of the theoretical.

Hydrocinnamamide is prepared by heating ammonium hydrocinnamate for five hours at 220°; it forms small, thin needles, which melt at 105°. When treated with bromine in alkaline solution, and then distilled with steam, it yields a mixture of phenylethylamine and a bromine-derivative, $C_8H_8Br·NH_2$, which boils at 252—254°. To obtain pure phenylethylamine the mixed product contained in the distillate is treated with sodium amalgam. The yield is about 30 per cent.

N. H. M.

Action of Ethyl Acetoacetate on the Amidines: Pyrimidines. By A. Pinner (*Ber.*, **18**, 2845—2852).—In order to test the general character of this reaction (Abstr., 1885, 158, 751), the author has tried to prepare the corresponding pyrimidines from various amidines, and he finds that, with the exception of formamidine, all the amidines experimented with are capable of yielding pyrimidines. When formamidine hydrochloride (25 grams) is treated with the calculated amount of ethyl acetoacetate, a 10 per cent. solution of sodium carbonate added, and the whole allowed to remain several weeks, a substance is obtained which crystallises in long, broad, silky needles, melting at 70—71°, is readily soluble in the ordinary solvents, with

the exception of water, and has neither acid nor basic properties; its composition indicates it to be *ethyl cyanoacetoacetate*,

$$CH_3{\cdot}C(CN):CH{\cdot}COOEt.$$

Acetamidine reacts readily with ethyl acetoacetate, yielding *dimethylhydroxypyrimidine*, $CMe\langle\begin{matrix}N\text{——}CMe\\N:C(OH)\end{matrix}\rangle CH$; this forms lustrous needles, melts at 192°, is readily soluble in water and alcohol, sparingly in ether and cold benzene. *Ethylmethylhydroxypyrimidine*, $C_7H_{10}N_2O$, obtained from propionamidine and ethyl acetoacetate, forms slender, white needles, melting at 160°, and readily soluble in water and alcohol. The hydrochloride, $C_7H_{10}N_2O,HCl$, crystallises in thick prisms, melts at 240—246° with decomposition, is very readily soluble in water, and somewhat less so in alcohol. The platinochloride forms thick, yellow prisms, melting at 236° with decomposition.

Succinimidine reacts with ethyl acetoacetate with elimination of only *one* molecule of water and production of a compound,

$$C_4H_4N_3H_2{\cdot}C_4H_5O_2.$$

A description is given of some more derivatives of phenylmethylhydroxypyrimidine (*loc. cit.*). When a solution of silver nitrate is added to a hot aqueous or alcoholic solution of the pyrimidine, a clear solution is obtained, from which ammonia throws down a white, granular precipitate of the silver salt; it is extremely soluble in excess of ammonia and in nitric acid. On adding bromine to a solution of phenylmethylhydroxypyrimidine in chloroform, four atoms of the halogen are taken up with formation of the compound $C_{11}H_{10}N_2OBr_4$, which crystallises in yellow, lustrous needles, melting at 245° with decomposition. It dissolves slowly with decomposition when boiled with alcohol, and on cooling, colourless, transparent needles of the composition $C_{11}H_9N_2Br$ separate, melting at 260°. Phenylmethylhydroxypyrimidine is not acted on by nascent hydrogen, but may be reduced by distillation with zinc-dust: the *phenylmethylpyrimidine*, $C_{11}H_{10}N_2$, obtained, melts at 74—78°, and yields a platinochloride, melting at 190° with decomposition. Chromic acid and alkaline potassium permanganate have little action on the hydroxycompound, whilst acid permanganate oxidises it readily with production of benzamide.

Attempts to reduce *phenylmethylchloropyrimidine*, $C_{11}H_9N_2Cl$ (Abstr., 1885, 159), by the action of sodium amalgam on its alcoholic solution, yielded *phemylmethylethoxypyrimidine*, $C_{11}H_9N_2{\cdot}OEt$, which, however, is more readily obtained by boiling the chloropyrimidine with sodium alcoholate. It forms thick, colourless, transparent prisms, melting at 30—31°, boils at 300—301°, is insoluble in water and alkalis, readily soluble in alcohol, ether, and acids. The *hydrochloride*, $C_{11}H_9N_2OEt,HCl + 2H_2O$, crystallises in slender, white, very soluble needles, and when dried melts at 148—149°; it breaks up at about 150° into phenylmethylhydroxypyrimidine and ethyl chloride. The *platinochloride*, $(C_{11}H_9N_2OEt)_2,H_2PtCl_6$, melts at 197° with decomposition. The *hydriodide*, $C_{11}H_9N_2OEt,HI(+\frac{1}{2}H_2O\ ?)$ forms yellow

prisms or long needles, very sparingly soluble in cold, moderately soluble in hot water; it melts at 143·5°.

Phenylmethylpyrimidineanilide, $C_{11}H_9N_2{\cdot}NHPh$, is obtained on heating the chloropyrimidine with aniline. The hydrochloride forms small slender needles which blacken at 236°, and melt with decomposition at 240°. The free base melts at 150—153°, and its nitrate at 85—87°. A. K. M.

Condensation of Acetoacetates with Bibasic Acids. By R. Fittig (*Ber.*, **18**, 2526—2527).—Ethereal acetoacetates condense readily with bibasic acids with elimination of 2 mols. H_2O. With succinic acid and ethyl acetoacetate, a crystalline compound, $C_{10}H_{12}O_5$, melting at 75·5—76°, is obtained. This is the monethyl salt of a bibasic acid, $C_8H_8O_5$; the free acid is crystalline, melts at 199—200°, and loses carbonic anhydride at a slightly higher temperature. From ethyl acetoacetate and sodium pyrotartrate the monethyl salt of the homologous acid, $C_9H_{10}O_5$, which melts at 194°, is obtained. The investigation of these acids is proceeding. A. J. G.

Condensation of Aldehydes with Bibasic Acids. By R. Fittig (*Ber.*, **18**, 2523—2525).—By the condensation of succinic acid with acetaldehyde, propaldehyde, isobutaldehyde, valeraldehyde, or œnanthaldehyde, a single lactonic acid is formed in each case, in accordance with the equation $X{\cdot}CHO + COOH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH = <^{O{\cdot}CHX}_{CO{\cdot}CH_2}>CH{\cdot}COOH$; with pyrotartaric acid, on the other hand, two isomeric lactonic acids,

$$<^{O{\cdot}CHX}_{CO{\cdot}CH_2}>CMe{\cdot}COOH \text{ and } <^{O\text{—}CHX}_{CO{\cdot}CHMe}>CH{\cdot}COOH,$$

are obtained. Benzaldehyde and pyrotartaric acid give in addition to the acid described by Penfield a second isomeric acid melting at 123·5°. These lactonic acids when heated lose carbonic anhydride, and are converted mainly into monobasic acids, the isomeric lactones being obtained as bye-products. The constitution of these unsaturated acids is still uncertain, except in the case of the acid $C_6H_{10}O_2$, derived from the lactonic acid prepared from propaldehyde and succinic acid, which has been shown to be identical with hydrosorbic acid.

Salicylaldehyde and succinic aldehyde yield a *dicoumarin*,

$$<^{C_6H_4{\cdot}CH}_{O\text{—}CO}>C{\cdot}C<^{CH{\cdot}C_6H_4}_{CO\text{—}O}>,$$

very similar in chemical behaviour to coumarin. Anisaldehyde and succinic aldehyde yield two acids of the formulæ

$$MeO{\cdot}C_6H_4{\cdot}CH : CH{\cdot}CH_2{\cdot}COOH \text{ and}$$
$$MeO{\cdot}C_6H_4{\cdot}CH : CH{\cdot}C(COOH) : CH{\cdot}C_6H_4{\cdot}OMe$$

respectively. No description is given of these substances.

A. J. G.

Tartronic Acids. By A. Pinner (*Ber.*, **18**, 2852—2854).—The author finds that no better yield of this acid is obtained by saponifying trichlorolactic acid directly with baryta water, and he prefers to use the method previously given (Abstr., 1885, 759). Experiments in which other precipitants (in the place of barium chloride) were employed, gave unsatisfactory results.

In the preparation of ethyl tartronate, only a part of the acid is converted into normal ethyl salt, some hydrogen ethyl-derivative being also probably formed. The normal salt boils at 222—225°, is readily decomposed by water, and is readily converted into the amide by the action of ammonia.

The only secondary products produced in the preparation of tartronic acid, which the author has been able to confirm, are dichloracetic acid, and a small quantity of oxalic acid.

Tartronamide, $CH{\cdot}OH(CONH_2)_2$, forms six-sided scales, melting at 195—196°, with decomposition. It is sparingly soluble in cold water, moderately in hot, and sparingly in alcohol. A. K. M.

Malic Acids. By H. van't Hoff, jun. (*Ber.*, **18**, 2713—2714; compare Abstr., 1885, 1201).—Inactive malic acid from monobromosuccinic acid, prepared from fumaric acid and hydrobromic acid (identical with that examined by Anschütz, *ibid.*, p. 1049), and an inactive malic acid obtained by the action of soda and water on maleic acid, are shown by crystallographic measurements to be identical with Pasteur's acid. N. H. M.

Decomposition of Malic Acid obtained from Fumaric Acid. By G. J. W. Beemer (*Rec. Trav. Chim.*, **4**, 180—182).—It is usually stated that the inactive malic acid obtained from fumaric acid is a distinct modification, and cannot be decomposed into the lævo- and dextro-acids. This is, however, not the case, as by the fractional crystallisation of its cinchonine salt, a malic acid is obtained, whose hydrogen ammonium salt shows a specific rotary power identical with that of the corresponding salt of the natural acid (*Ber.*, **13**, 352). A. P.

Constitution of Isosaccharic Acid. By H. Kiliani (*Ber.*, **18**, 2514—2518).—In the author's last paper on this subject (Abstr., 1885, 744), the position of one of the hydroxyl-groups was still left unsettled; he now shows that the dihydroxypropenyltricarboxylic acid obtained by oxidising isosaccharic acid (*loc. cit.*) yields a dihydroxyglutaric acid, not identical with the β-γ-dihydroxy-acid; this must therefore be the α-γ-acid,

$$COOH{\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}COOH.$$

From this isosaccharic acid must have the constitution

$$COOH{\cdot}C(OH)(CH_2{\cdot}OH){\cdot}CH_2{\cdot}CH(OH){\cdot}COOH.$$

α-γ-Dihydroxyglutaric acid is best obtained by heating dihydroxypropenyltricarboxylic acid for four hours at 120°. It crystallises in colourless prisms, begins to soften at 106° with loss of water, and only fuses completely at a considerably higher temperature; it is

nearly insoluble in ether, readily soluble in alcohol and water. The calcium salt, $C_5H_6O_6Ca + 3H_2O$, forms white nodular crystals, sparingly soluble in water.

β-γ-Dihydroxyglutaric acid, $COOH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}COOH$, is obtained by converting glutaconic acid,

$$COOH{\cdot}CH_2{\cdot}CH{:}CH{\cdot}COOH,$$

into dibromoglutaric acid, by treatment with bromine, and boiling the product in dilute solution for two hours and a half with calcium carbonate. It crystallises in needles or six-sided plates, melts at 155—156°, and is sparingly soluble in alcohol, very readily soluble in water. It is further distinguished from the α-γ-acid by the ready solubility of its calcium and cadmium salts. A. J. G.

Oxidation of Benzene. By J. G. Holder (*Amer. Chem. J.*, **7**, 114—116).—When treated in the cold with manganese dioxide and sulphuric acid, benzene yields carbonic anhydride and a small quantity of benzoic acid; neither formic nor phthalic acid could be detected. By gradually adding sulphuric acid to benzene and lead dioxide, a vigorous reaction occurs, and carbonic anhydride and benzoic acids are formed; no succinic acid was observed. Potassium permanganate acts very slowly; lead dioxide and boiling dilute nitric acid yield only oxalic acid; chromic acid yields only carbonic anhydride. H. B.

Parachlorometanitrotoluene and its Reduction-products. By L. Gattermann and A. Kaiser (*Ber.*, **18**, 2599—2602).—This compound was prepared from metanitroparatoluidine hydrochloride by treatment with cuprous chloride and sodium nitrite. It crystallises in yellow needles, melts at 7° to a strongly refractive, golden-yellow oil, of sp. gr. 1·297 at 22° (water at 22° = 1), and boils at 260—261° under 745 mm. pressure. It seems to be identical with the α-nitro-compound obtained by Wroblewsky by the direct nitration of parachlorotoluene.

Parachlorometanitrotoluidine, $C_6H_3MeCl{\cdot}NH_2$, obtained by reduction of the nitro-compound, crystallises in thin, colourless tables, melts at 29—30°, and has an odour similar to that of naphthylamine. The hydrochloride crystallises in colourless needles, the sulphate in broad needles or plates; the acetyl compound crystallises in colourless needles, and melts at 96°. A. J. G.

Action of Phenyl Cyanate on Polyhydric Alcohols. By H. Tesmer (*Ber.*, **18**, 2606—2610, compare Abstr., 1885, 774).—The author confirms the formula $C_6H_9O(O{\cdot}CO{\cdot}NHPh)_3$, previously given for the quinovide of phenylcarbamic acid.

Quercyl pentaphenylcarbamate, $C_6H_7(O{\cdot}CO{\cdot}NHPh)_5$, is prepared by heating quercite and phenyl cyanate in sealed tubes at 165° for two hours; it is an amorphous white mass, melts somewhere between 120—140°, and is soluble in the ordinary solvents except light petroleum. When heated with aqueous baryta at 150°, it is decomposed into aniline, quercite, and carbonic anhydride.

Saccharyl phenylcarbamate, $C_6H_7O_2(O{\cdot}CO{\cdot}NHPh)_3 + CONPh$, pre-

pared in a similar manner from saccharin, crystallises in silky, interlaced needles, melts at 230—240° with decomposition. It is sparingly soluble in benzene and alcohol, soluble in ether, readily soluble in aniline; aqueous baryta at 160—170° converts it in aniline and barium carbonate and saccharate.

Metasaccharyl phenylcarbamate, $C_6H_7O_2(O{\cdot}CO{\cdot}NHPh)_3 + CONPh$, is obtained as an amorphous, white powder, which softens at 205°, melts about 210°, and is soluble in most solvents. With aqueous baryta, it yields aniline, and barium carbonate and metasaccharate.

Isosaccharyl phenylcarbamate, $C_6H_7O_2(O{\cdot}CO{\cdot}NHPh)_3 + CONPh$, also forms an amorphous, white powder, softens at 180°, and melts at 181°; with aqueous baryta, it is decomposed in the same manner as the preceding compounds.

Quercetyl phenylcarbamate, $C_{24}H_{11}O_6(O{\cdot}CO{\cdot}NHPh)$, prepared by heating quercetin and phenyl cyanate at 160°, is a pale yellow, amorphous mass. It melts at 200—205°, and is insoluble in most solvents. Aqueous baryta at 170° decomposes it into quercetin, aniline, and barium carbonate.

Flavopurpuryl phenylcarbamate, $C_{14}H_6O_3(O{\cdot}CONHPh)_2$, is prepared by heating flavopurpurin and phenyl cyanate at 165°; it crystallises in yellowish, microscopic plates, insoluble in most solvents; boiling aniline dissolves it, with formation of flavopurpurin and diphenylcarbamide; alkalis resolve it into flavopurpurin, aniline, and carbonic anhydride. A. J. G.

Para- and Meta-phenylene Cyanate. By L. Gattermann and E. Wrampelmeyer (*Ber.*, **18**, 2604—2606).—*Paraphenylene cyanate*, $C_6H_4(N:CO)_2$, is prepared by the action of carbonyl chloride on paraphenylenediamine; it crystallises in white needles, melts at 91°, boils at 231° under 745 mm. pressure. It shows a close resemblance in reactions and properties to phenyl cyanate, giving paraphenylenedicarbamide with ammonia, diphenylphenylenedicarbamide with aniline, &c. When heated with absolute alcohol, it yields *paraphenyleneurethane*, $C_6H_4(NH{\cdot}COOEt)_2$, which crystallises in colourless prisms, and melts at 193°. Paraphenylenecarbamide is also formed in the preparation of paraphenylene cyanate.

Metaphenylene cyanate is prepared in similar manner to, and closely resembles the para-compound. A. J. G.

Resorcinol-derivatives. By G. Errera (*Gazzetta*, **15**, 261—274).—*Trinitrodibenzoylresorcinol*, $NO_2{\cdot}C_6H_3(O{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2)_2$, obtained by the action of nitric acid (sp. gr. 1·4) on dibenzoylresorcinol, is a yellow, amorphous substance, melting at 123—124°, insoluble in water, sparingly soluble in alcohol, readily in benzene and chloroform. It is not decomposed by hydrochloric acid, but is saponified completely by alcoholic potash into nitroresorcinol, together with iso-dinitroresorcinol and metanitrobenzoic acid, or the latter and benzoic acid, according to the conditions of the experiment. The nitroresorcinol and metanitrobenzoic acid can be separated by treatment with acetic chloride, or by the different solubility of the copper salts, or by the etherification of the acid.

Trinitrodibenzoylresorcinol is reduced by tin and hydrochloric acid to amidoresorcinol and amidobenzoic acid.

Mononitrodibenzoylresorcinol, $NO_2 \cdot C_6H_3(OBz)_2$, prepared either by the action of zinc-dust on a mixture of nitroresorcinol (1 mol.) with benzoic chloride (2 mols.), or by the nitration of dibenzoylresorcinol by a mixture of nitric and sulphuric acids, crystallises in acicular needles, melting at 110°; on hydrolysis, it yields mononitroresorcinol and benzoic acid, and on reduction benzoic acid and amidoresorcinol.

Mononitromonobenzoylresorcinol, $NO_2 \cdot C_6H_3(OH) \cdot OBz$, obtained by heating a mixture of nitroresorcinol and benzoic chloride in equimolecular proportions, crystallises in pale-yellow needles.

Mononitrodiacetylresorcinol, $NO_2 \cdot C_6H_3(OAc)_2$, from acetic chloride and nitroresorcinol, forms long lamellar colourless crystals, melting at 90—91°; it is converted by bromine into Weselsky's dibromonitroresorcinol. V. H. V.

Fluoresceïns from Maleic Acid. By R. Burckhardt (*Ber.*, **18**, 2864—2870).—This is a continuation of the work published by Lunge and Burckhardt (Abstr., 1884, 1340).

Dimethylmaleïnfluoresceïn, $O<\begin{matrix}C_6H_3(OMe)\\C_6H_3(OMe)\end{matrix}>C<\begin{matrix}CH:CH\\O—CO\end{matrix}>$, is formed when a solution of maleïnfluoresceïn in methyl alcohol is boiled with alcoholic potash and methyl iodide, and crystallises in red needles. Unsuccessful attempts were made to obtain a bromine-derivative corresponding with eosin, but no definite product could be obtained. Maleïnfluoresceïn reacts with acetic chloride, yielding a *diacetyl-derivative*, $C_{16}H_{10}O_6Ac_2$, crystallising in yellowish-white needles, melting at 157°; it is sparingly soluble in alcohol, readily in glacial acetic acid, and insoluble in water, chloroform, carbon bisulphide, and benzene.

α-Naphtholmaleïnfluoresceïn, $<\begin{matrix}CH:CH\\CO—O\end{matrix}>C(C_{10}H_6 \cdot OH)_2$, obtained on heating maleic anhydride (1 mol.) with α-naphthol (2 mols.) and zinc chloride at 160°, forms a violet powder, which yields a red solution with alcohol, the addition of ammonia producing an intense green-red fluorescence; the solution changes on exposure to the air, becoming first violet, and then dirty brown. The compound is also soluble in ether, glacial acetic acid, chloroform, ethyl acetate, and methyl alcohol, but is insoluble in benzene and carbon bisulphide. It melts at 118—120°. A second compound, $C_{14}H_{10}O_4$, is formed simultaneously with the last substance by the union of maleic anhydride (1 mol.) with α-naphthol (1 mol.). It crystallises in small, hygroscopic needles melting at 90°, dissolves in the ordinary solvents with the exception of benzene, toluene, and carbon bisulphide; also in hydrochloric acid, water, and ammonia. It forms a lead salt of the composition $C_{28}H_{18}PbO_4$.

β-Naphthol yielded no fluorescent product with maleic anhydride, the statement previously made (*loc. cit.*) referring to the employment of fumaric acid. The product of the latter reaction forms a yellow solution with alcohol, which exhibits an intense moss-green fluorescence on the addition of ammonia.

The reactions of several other phenols with maleic anhydride have also been tested qualitatively. A. K. M.

Chloro- and Bromo-derivatives of Phloroglucinol. By K. Hazura and R. Benedikt (*Monatsh. Chem.*, **6**, 702—707).—*Hexabromophloroglucinol dibromide*, $C_6Br_3(OBr)_3,Br_2$, is obtained together with phlorobromine when a solution of 10 grams of phloroglucinol in 1 litre of water (at 40°) is treated with 96 grams of bromine, added 24 grams at a time. It dissolves very readily in chloroform, from which it crystallises in small, yellowish-white needles melting at 118°. Sulphurous acid converts it into tribromophloroglucinol melting at 151°. When heated at 156°, it gives off a part of its bromine.

Hexahydrotrichlorophloroglucinol, $C_6H_9Cl_3O_3+3H_2O$, is prepared from the above compound by the action of tin and hydrochloric acid; it forms long, white crystals which melt at 125°. At 100° it loses its water of crystallisation.

Trichlorophloroglucinol, $C_6Cl_3H_3O_3+3H_2O$, is prepared by the action of chlorine on a solution of phloroglucinol in glacial acetic acid. It softens when heated at 120°, and melts at 129°. At 100° it loses 3 mols. of water. N. H. M.

Thymolphosphoric Acids. By G. Discalzo (*Gazzetta*, **15**, 278—282).—*Monothymolphosphonyl chloride*, $POCl_2{\cdot}O{\cdot}C_6H_3MePr$, prepared by heating a mixture of phosphorus oxychloride and thymol in equimolecular proportions, is a colourless, mobile liquid, boiling with slight decomposition at 280—285°. When heated with water, it is converted into the corresponding *acid*, $PO(OH)_2{\cdot}O{\cdot}C_6H_3MePr$, a thick, oily liquid, sparingly soluble in water, soluble in alkalis, decomposed completely on distillation into thymol and metaphosphoric acid. Its *barium* salt crystallises in prismatic laminæ.

Dithymolphosphonyl chloride, $POCl(OC_6H_3MePr)_2$, prepared from a mixture of thymol (2 mols.) with phosphorus oxychloride (1 mol.), is a colourless, fluorescent liquid, boiling at 330—340°, under a pressure of 320 mm. It is decomposed by water, forming *dithymolphosphoric* acid, $PO(OH)(O{\cdot}C_6H_3MePr)_2$. This substance is insoluble in water; its *barium* salt crystallises with $5H_2O$ in delicate, colourless needles. V. H. V.

Nitration of Parabromaniline. By H. Hager (*Ber.*, **18**, 2578).—When parabromaniline is nitrated, the bromine-atom is displaced and picramide (trinitraniline) formed. A. J. G.

Action of Isbutyric Acid on Aniline. By F. L. Bardwell (*Amer. Chem. J.*, **7**, 116—118).—Aniline and isobutyric acid do not react with each other until zinc chloride is added, when *isobutyranilide* is formed; the yield is increased by heating the mixture. It crystallises in colourless prisms and melts at 102·5°. By the action of bromine-vapour on the aqueous solution, a yellow precipitate is formed, which when treated in alcoholic solution with charcoal yields colourless needles of *parabromisobutyranilide*, $C_6H_4Br{\cdot}NHC_4H_7O$; it melts at 128°, and when heated with aqueous hydrochloric acid yields para-

bromaniline; treated with nitric and sulphuric acids it yields para-bromorthonitraniline. H. B.

Metadinitroazoxybenzene and Orthazoxytoluene. By H. KLINGER and H. PITSCHKE (*Ber.*, **18**, 2551—2556).—*Metadinitroazoxybenzene*, $NO_2{\cdot}C_6H_4{\cdot}N_2O{\cdot}C_6H_4{\cdot}NO_2$, is obtained by treating metadinitrobenzene with a small quantity of sodium methoxide dissolved in methyl alcohol. It crystallises in long, straw-yellow needles, melts at 141—142°, is sparingly soluble in alcohol, somewhat more soluble in ether and carbon bisulphide, moderately soluble in benzene and toluene.

Metadinitrohydroxyazobenzene, $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(OH){\cdot}NO_2$, is obtained by heating a solution of the azoxy-compound in sulphuric acid at 140°; it forms a yellowish-brown, indistinctly crystalline mass, and melts at 172—173°. It dissolves in dilute alkalis with yellowish-red colour. The silver salt, $C_{12}H_7N_4O_4{\cdot}OAg$, is obtained as a red, crystalline precipitate.

Orthazoxytoluene, $C_6H_4Me{\cdot}N_2O{\cdot}C_6H_4Me$, is prepared by the action of sodium methoxide on orthonitrotoluene; it crystallises in yellow, monosymmetric tables or needles, $a : b = 0{\cdot}84158 : 1$; $\beta = 68°\ 37'$; observed faces, 0P, $\infty P\infty$, ∞P; melts at 59—60°, and explodes when more strongly heated. When distilled with iron, it yields orthazotoluene together with a little orthotoluidine. When heated with sulphuric acid, it undergoes a peculiar decomposition, much orthazotoluene being formed (44—48 per cent.) together with amorphous substances. A. J. G.

Methylene-Blue Group. By A. BERNTHSEN (*Annalen*, **230**, 73—211).—A considerable portion of this research has already appeared in this Journal (Abstr., 1883, 916; 1884, 595, 1156; 1885, 259). *Leucothionine* or *diamidothiodiphenylamine*,

$$NH<\begin{matrix}C_6H_3(NH_2)\\C_6H_3(NH_2)\end{matrix}>S \quad [NH_2 : NH : NH_2 : S = 4 : 1 : 4 : 6],$$

is formed by the action of tin and hydrochloric acid on α-dinitrodiphenylamine sulphoxide. Under similar treatment, β-dinitrodiphenylamine sulphoxide, $NH<\begin{matrix}C_6H_3(NO_2)\\C_6H_3(NO_2)\end{matrix}>SO$, yields *leuco-isothionine*, $C_6H_4<\begin{matrix}-S-\\NH\end{matrix}>C_6H_2(NH_2)_2$. On oxidation with ferric chloride, *isothionine*, $NH<\begin{matrix}C_6H_2(NH_2)\\|\\N{\cdot}C_6H_4\end{matrix}>S$, is produced. It is a dark, crystalline powder, sparingly soluble in water and freely soluble in alcohol, yielding violet-red solutions. It dissolves sparingly in warm benzene, forming an orange-coloured liquid. The *hydrochloride*, $C_{12}H_9N_3S,2HCl$, is freely soluble in water and alcohol. The aqueous solution is violet-red, and dyes silk amethyst. The addition of strong hydrochloric acid does not turn the solution blue, as is the case with thionine. The salt dissolves in strong sulphuric acid with violet coloration.

The composition of methylene-blue was ascertained from the analysis of the hydriodide, $C_{16}H_{18}N_3SI$, and the hydrochloride,

$C_{16}H_{18}N_3SCl + 3H_2O$. The aqueous solution of the free base (tetramethylthionine hydroxide) is obtained by treating a dilute solution of the hydriodide with freshly precipitated silver oxide. On evaporating the solution in a vacuum over sulphuric acid at the ordinary temperature, the free base remains as a dark, amorphous mass. It dissolves freely in alcohol and in water. The preparation and properties of leucomethylene-blue (formerly called methylene-white) have been already described (Abstr., 1883, 916). *Pentamethylleucothionine-dimethiodide*, $C_{17}H_{21}N_3S,2MeI$, is formed by the action of methyl iodide and methyl alcohol on leucomethylene blue at 110°. The compound is soluble in hot water, but insoluble in ether. It is decomposed by moist oxide of silver, yielding the ammonium base,

$$NM_2<\begin{matrix}C_6H_3(NMe_3\cdot OH)\\C_6H_3(NMe_3\cdot OH)\end{matrix}>S.$$

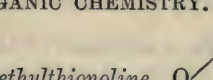
On evaporating the alkaline liquid, the base remains as a brittle, amorphous mass, soluble in alcohol and in water. It is decomposed by heat, yielding methyl alcohol and pentamethylleucothionine. The constitution of leucomethylene-blue, or tetramethylparadiamidothiodiphenylamine is proved to be

$$NH<\begin{matrix}C_6H_3\cdot NMe_2\\C_6H_3\cdot NMe_2\end{matrix}>S \quad [NH : NMe_2 = 1 : 4],$$

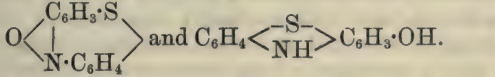
by the fact that it yields on methylation the same pentamethylleucothioninedimethylammonium iodide, which is obtained from leucothionine. The free base of methylene-blue is represented by the formula $HO\cdot NMe_2<\begin{matrix}C_6H_3\text{———}S\\|\\N\cdot C_6H_3(NMe)\end{matrix}>$.

Methylene-red is obtained as a bye-product in the preparation of methylene-blue. It is contained in the mother-liquor from which the methylene-blue has been precipitated. The pure compound is deposited from alcohol in glistening green prisms, soluble in water. The aqueous and alcoholic solutions exhibit a purple colour, which disappears on the addition of an alkali. The colour does not reappear on acidification. A blue colour is produced by oxidation. Reducing agents also destroy the purple colour, and in this case sulphuretted hydrogen is liberated. The hydrochloride of methylene-red has the composition $C_{16}H_{18}N_4S_4,2HCl$. On the addition of ammonia to methylene-red, a yellow-coloured base is precipitated. It is soluble in alcohol and in ether. It is precipitated from the alcoholic solution by water.

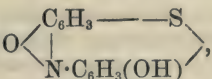
When methylene-blue is treated with a dilute solution of an alkali, a mixture of methylene-violet, methylene-azure, leucomethylene-blue, and other leuco-products is formed. Methylene-violet is best obtained in the pure state by decomposing methylene hydriodide with silver oxide, and boiling the aqueous solution of the base for several hours. The solution deposits crystals of pure methylene-violet, and the mother-liquor contains methylene-azure. The precipitate of silver iodide is mixed with a considerable quantity of leuco-bases.

Methylene-violet or *dimethylthionoline*,  , is deposited from alcohol in long needles, soluble in chloroform and sparingly soluble in hot water. The solutions have a red or violet-red colour and are fluorescent. The hydrochloride, $C_{14}H_{12}N_2SO,HCl$, crystallises in long needles of a dark green colour. It is insoluble in cold dilute hydrochloric acid. The aqueous solution dyes wool or silk violet. The iodide and chromate are very slightly soluble in hot water; in other respects, they resemble the corresponding salts of methylene-blue. *Leucomethylene-violet* is deposited from alcohol in white plates or scales. The solution in acids is stable, but the solution in alkalis absorbs oxygen with great avidity, and deposits methylene-violet. The hydrochloride is crystalline. In order to obtain *methylene-azure* in a state of purity, the mother-liquor from which the methylene-violet has been deposited is treated with an alkaline solution of stannous chloride. The liquid is mixed with half its volume of alcohol, and left for some time in a closed vessel. The leuco-azure which is deposited as a crystalline mass is washed, dissolved in dilute hydrochloric acid, and oxidised by ferric chloride. On the addition of common salt, methylene-azure is precipitated. It is dissolved in water, reprecipitated and converted into the hydriodide. This salt is more soluble in water than methylene-blue hydriodide, which it closely resembles. The hydrochloride is also very soluble in water. The solution dyes silk blue. The hydrochloride dissolves in strong hydrochloric acid with a blue coloration, and in strong sulphuric acid with a green colour. It is decomposed by boiling with a strong solution of potassium hydroxide, with formation of dimethylamine.

The preparation of *oxythiodiphenylimide* and *hydroxythiodiphenylamine* has been already described (Abstr., 1885, 260). The constitution of these compounds may be represented by the formulæ—



Silk immersed in an alkaline solution of the latter compound is dyed crushed strawberry.

Thionol or *dioxythiodiphenylimide*,  , is prepared by treating thiodiphenylamine with sulphuric acid diluted with one-fifth its weight of water at 160° for 24 hours. The product of the reaction is poured into water, mixed with excess of sodium hydroxide, and filtered. On the addition of hydrochloric acid to the hot filtrate, *thionol hydrochloride* is deposited in glistening green crystals.

The free base is insoluble in cold water, but dissolves freely in acids. It is deposited from glacial acetic acid in plates. The alcoholic solution is of a purple colour, and the solution in strong sulphuric acid is blue. The sulphate, $2C_{12}H_7NSO_2,H_2SO_4$, forms green needles. The barium salt, $C_{12}H_7NSO_3Ba$, crystallises in plates exhibiting a green

lustre. Silk immersed in a solution of thionol in potassium carbonate acquires a violet colour which turns red on exposure to the air. Thionol is formed in small quantities by the continued action of alkalis on methylene-blue; it is also a product of the action of alkalis, or of strong sulphuric acid on thionine.

Leucothionol, $NH<\begin{matrix}C_6H_3(OH)\\C_6H_3(OH)\end{matrix}>S$, is formed by treating an ammoniacal solution of thionol with zinc-dust. It is deposited from its ethereal solution as a crystalline, colourless mass. On treatment with acetic anhydride, it yields a triacetyl derivative.

Thionoline, $O<\begin{matrix}C_6H_3\text{———}S\\|\qquad\quad\ \ \backslash\\N{\cdot}C_6H_3(NH_2)\qquad\ \ >\end{matrix}$, is formed by adding ferric chloride to amidophenol which has been saturated with sulphuretted hydrogen. It is also produced by the prolonged boiling of thionine in water, $NC_{12}H_6S(NH_2)NH + H_2O = NC_{12}H_6S(NH_2)O + NH_3$.

Thionoline dissolves in hot alcohol, forming a purple solution; the leuco-compound, $NH<\begin{matrix}C_6H_3(NH_2)\\C_6H_3(OH)\text{-}\end{matrix}>S$, is soluble in acids and in alkalis. The nitrate, sulphate, and hydrochloride of thionoline crystallise in needles. Strong sulphuric acid dissolves thionoline, forming a blue solution. Methylene-violet is dimethylthionoline. W. C. W.

Benzyl Compounds. By O. Borgmann (*Chem. Centr.*, 1885, 456—458).—This communication contains an account of several metabenzyl compounds, prepared from metanitrobenzyl alcohol, some of which have already been described (Abstr., 1883, 1121).

Primary metanitrobenzylamine, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH_2$, is formed by treating metanitrobenzyl chloride with alcoholic ammonia; it is a yellowish oil, absorbs carbonic anhydride from the air, forming a solid salt, and yields a sparingly soluble oxalate and platinochloride. The *secondary* amine, $NH(NO_2{\cdot}C_6H_4{\cdot}CH_2)_2$, formed with the primary, crystallises in yellowish, rhombic leaflets, melting at 87°; its hydrochloride and platinochloride are both sparingly soluble salts. When reduced by tin and hydrochloric acid, it forms an amido-compound, the hydrochloride of which crystallises from concentrated hydrochloric acid in long, reddish needles, having the composition $N(NH_2{\cdot}C_6H_4{\cdot}CH_2)_2{,}3HCl$. The base crystallises in prisms melting at 86—87°.

Tertiary metanitrobenzylamine, $N(NO_2{\cdot}C_6H_4{\cdot}CH_2)_3$, is formed by digesting metanitrobenzyl chloride with aqueous ammonia; it crystallises in monoclinic prisms, melts at 162°, is soluble in glacial acetic acid and benzene, but only sparingly in alcohol, is insoluble in ether, and does not unite with hydrochloric acid. When reduced with tin and hydrochloric acid, it yields the tertiary *amido*-compound, which crystallises in colourless needles, melts at 142°, and forms a sparingly soluble platinochloride.

Amidobenzyl chloride is very unstable and is formed by the reduction of the nitro-compound with tin and hydrochloric acid.

Metanitrodibenzylmethylamine, $NMe(NO_2{\cdot}C_6H_4{\cdot}CH_2)_2$, is formed by acting on nitrobenzyl chloride with an aqueous solution of methylamine; it melts at 81°. By the action of dimethylamine, *metanitro-*

benzyldimethylamine, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NMe_2$, is formed; it is a yellowish oil, and forms a well-defined platinochloride.

Metanitrobenzylphenylamine, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NHPh$, is formed by the action of aniline on nitrobenzyl chloride; it crystallises in long, orange-red needles, melting at 86°; its hydrochloride forms white leaflets, is an unstable compound, and does not form a platinochloride. When reduced by tin and hydrochloric acid, this base forms *metamidobenzylphenylamine*, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot NHPh$, melting at 67°.

Metanitrobenzaldehyde, when treated with concentrated sodium hydroxide, yields meta-azoxybenzoic acid, $ON_2(C_6H_4 \cdot COOH)_2$.

P. P. B.

Ethylortholuidines. By R. L. Chase (*Amer. Chem. J.*, **7**, 118—120).—These compounds have been prepared by Reinhardt and Staedel (Abstr., 1883, 578). Ethylortholuidine, formed from ethyl iodide and orthotoluidine, boils at 204—206°; its salts are exceedingly soluble in water; the chloride, platinochloride, iodide, acetyl- and nitroso-compounds are mentioned.

Diethylorthotoluidine was prepared from the monethyl-derivative and ethyl iodide, it boils between 203—208°; the hydriodide crystallises well from water, it contains 1 mol. H_2O. H. B.

Consecutive Orthoxylidine and Orthoxylenol. By A. Töhl (*Ber.*, **18**, 2561—2562).—*Mononitrodibromortho-xylene*, $C_6HMe_2Br_2 \cdot NO_2$ [$Me_2 : Br_2 : NO_2 = 1 : 2 : 3 : 4 : 5$], is obtained together with the dinitro-compound by adding 4, 5 dibromortho-xylene to cold fuming nitric acid. It crystallises in colourless needles, and melts at 141°. *Dinitrodibromortho-xylene*, $C_6Me_2Br_2(NO_2)_2$, crystallises in small needles, and melts at about 250°.

Dibromortho-xylidine, $C_6HMe_2Br_2 \cdot NH_2$, is prepared from the mononitro-derivative by heating it with iron and acetic acid. It crystallises in colourless needles, melts at 103°, distils with steam, is readily soluble in alcohol, ether, and glacial acetic acid, and does not yield salts with acids. The bromine is, to a great extent, removed by long treatment with tin and hydrochloric acid, but complete replacement can only be effected by the action of sodium amalgam on a warm alcoholic solution.

Ortho-xylidine, $C_6H_3Me_2 \cdot NH_2$ [$Me : Me : NH_2 = 1 : 2 : 3$], so obtained, is a colourless oil, which turns brown on long exposure to air, does not solidify at − 15°, and boils at 221—222°. The hydrochloride, $C_6H_3Me_2 \cdot NH_2,HCl + H_2O$, crystallises in large, lustrous tables, and sublimes readily; the nitrate and sulphate are also described. *Acetxylide*, $C_6H_3Me_2 \cdot NHAc$, crystallises in long, slender needles, and melts at 131°.

Ortho-xylenol, $C_6H_3Me_2 \cdot OH$ [$Me_2 : OH = 1 : 2 : 3$], prepared in the usual way from the xylidine, crystallises in very long, slender needles, melts at 75°, boils at 218°, and yields a blue coloration with ferric chloride in aqueous solution. The *tribromo*-derivative, $C_6Me_2Br_3 \cdot OH$, crystallises in slender needles, and melts at 184°. A. J. G.

Paraxylidine. By E. Nölting, O. Witt, and S. Forel (*Ber.*, **18**, 2664—2668).—Crude xylidine was found to contain about 25 per cent.

of paraxylidine boiling at 215° under 739 mm. pressure. Sp. gr. = 0·980 (water at 15° = 1). *Nitraceto-xylide*, melting at 166°, is obtained by nitrating the acetyl-derivative; it yields a *nitro-xylidine* which melts at 142°, and crystallises from benzene in brownish-yellow, lustrous crystals, readily soluble in alcohol and ether. When nitro-xylidine is reduced *xylenediamine* is formed; this crystallises from benzene in small white needles melting at 146·5—147°, which, when oxidised, yield paraxyloquinone.

Ethyl nitrite acts on nitro-xylidine with formation of the *ethyl salt* of nitroparaxylenol; it is a yellow substance melting at 85°.

N. H. M.

The Six Isomeric Xylidines. By E. Nölting and S. Forel (*Ber.*, **18**, 2668—2681).—A description of these compounds and some derivatives is given. When consecutive ortho-xylidine is oxidised it yields *ortho-xyloquinone*, $C_6H_2Me_2O_2$ [$Me_2 : O_2 = 1 : 2 : 3 : 6$]. This compound sublimes in yellow needles which melt at 55°; it is rather readily soluble in alcohol, ether, &c. It is reduced by sulphurous acid to the *quinol*, a white substance, melting at 221°. *Ortho-xylenol* [$Me_2 : OH = 1 : 2 : 3$], is obtained from the diazo-derivative of the base; it crystallises from water in white needles, melts at 73°, and sublimes unchanged. The aqueous solution acquires a pale-violet colour when treated with ferric chloride.

Metaxylylquinone, $C_6H_2Me_2O_2$ [$Me_2 : O_2 = 1 : 3 : 2 : 5$] is prepared by oxidising metaxylidine; it forms splendid, yellow needles which melt at 73°. The corresponding *quinol* forms white needles melting at 149°. When symmetrical metaxylidine is nitrated, a *nitro-derivative* [$Me_2 : NH_2 : NO_2 = 1 : 3 : 5 : 4$] melting at 54° is formed; this, when reduced, yields metaxyleneorthodiamine, melting at 77°.

When the hydrochlorides of the xylidines are heated with methyl alcohol at 300—320°, amidotrimethylbenzenes are formed. Consecutive ortho-xylidine yields a liquid *amidotrimethylbenzene* boiling at 240°; the *acetyl-derivative* melts at 180°. Symmetrical metaxylidine yielded a crystalline *isocumidine* which melts at 67—68°, and boils at 245° (uncorr.); the *acetyl-derivative* melts at 163—164°; the cumenol melts at 98—99°.

N. H. M.

Amidoazo-derivatives of the Three Xylenes. By E. Nölting and S. Forel (*Ber.*, **18**, 2681—2686). — *Amidoazometaxylene*, $C_6H_3{\cdot}Me_2{\cdot}N_2{\cdot}C_6H_2Me_2{\cdot}NH_2$ [$Me : Me : N_2 : Me : NH_2 : Me = 4 : 2 : 1 : 2 : 3 : 4$], is prepared by the action of 69 grams of a 20—25 per cent. solution of sodium nitrite on a well-cooled mixture of 121 grams metaxylidine and 157 grams metaxylidine hydrochloride. The product is extracted with ether, and the residue left on evaporating the ether is warmed with 120 grams of metaxylidine and 10—15 grams of metaxylidine hydrochloride at about 50°. It is then boiled with dilute hydrochloric acid, and the sparingly soluble hydrochloride thus obtained is washed with water, alcohol, and ether. The base is liberated by means of ammonia and crystallised from alcohol or benzene. It forms orange-yellow plates which melt at 78°, is almost insoluble in water, readily soluble in hot alcohol and in benzene. The *hydrochloride* forms a bright yellow crystalline powder; its alcoholic

solution is green. When reduced, it yields a diamine melting at 77—78°.

Amido-azometaxylene, [Me:Me:N_2:Me:Me:NH_2 = 6:2:1:3:5:4], crystallises in yellow plates melting at 77·5°; it dissolves readily in alcohol and in benzene. The alcoholic solution of the *hydrochloride* is red.

Amido-azometaxylene, [N_2 : Me : Me : NH_2 = 1 : 2 : 6 : 4], crystallises from alcohol in yellow plates melting at 95°. The solution of the *hydrochloride* in phenol is violet.

Amido-azortho-xylene, [Me : Me : N_2 : Me : Me : NH_2 = 3 : 2 : 1 : 2 : 3 : 4], forms yellow plates, and melts at 110·5°.

Amido-azortho-xylene, [Me : Me : N_2 : Me : Me : NH_2 = 6 : 3 : 1 : 4 : 5 : 2], forms yellow plates melting at 179°; it is sparingly soluble in alcohol. The solution of the hydrochloride in phenol is green.

Amido-azoparaxylene, [Me : Me : N_2 : Me : Me : NH_2 = 5 : 2 : 1 : 3 : 6 : 4], crystallises from alcohol in red plates melting at 150°. The *hydrochloride* is red; its solution in phenol is violet-red. When the base is reduced, a *diamine* melting at 146·5—147° is formed.

Experiments made by the authors show that the amidoazoxylene described by Nietzki (Abstr., 1880, 552) is a mixed *amidoazo-metaparaxylene* [Me : Me : N_2 : Me : Me : NH_2 = 4 : 2 : 1 : 3 : 6 : 4]; it melts at 110—111°. N. H. M.

Azo-derivatives of Carvacrol. By G. Mazzara (*Gazzetta*, **15**, 305—315).—In continuation of experiments on the azo-derivatives of thymol and carvacrol (Abstr., 1885, 904 and 1132), the author describes the preparation of an azo-compound by heating 1 mol. of bidiazotriphenylmethane with 2 mols. carvacrol dissolved in potash. There is thus formed a purplish-red, amorphous substance, carvacrol-bidiazotriphenylmethane, to which is ascribed the composition [$OH{\cdot}C_6H_2MePh{\cdot}N_2{\cdot}C_6H_4{\cdot}CHPh{\cdot}C_6H_4{\cdot}N_2,C_6H_2MePh]_2O$. It melts at 130°, and is soluble in ether and chloroform; its potassium-derivative is a red precipitate; when heated with bidiazobenzene it is converted into a red crystalline substance, the composition of which has not yet been definitely established. V. H. V.

Derivatives of Diphenylurethane. By H. Hager (*Ber.*, **18**, 2573—2577).—Diphenylurethane is best obtained by heating diphenylamine with ethyl chlorocarbonate.

Di-orthonitrophenylurethane, $(NO_2{\cdot}C_6H_4)_2N{\cdot}COOEt$, is obtained together with the para-compound by adding diphenylurethane to nitric acid of sp. gr. 1·44, and pouring the solution into much water; the mixture is separated by treatment with a little hot benzene, from which the para-compound crystallises on cooling. The ortho-compound forms a brown syrupy mass readily soluble in alcohol, and seems to be miscible in all proportions with benzene. Potash converts it into orthonitrodiphenylamine. When heated alone, it yields a mixture of products from which a colourless liquid, boiling at 141—143° and of the formula $C_8H_{10}O$, was isolated. This is insoluble in water, readily soluble in ether, and unites with bromine to form a yellow liquid, yielding on distillation an oil which gives a nitro-derivative melting at 181—182°.

Di-paranitrophenylurethane crystallises in yellow needles, melts at 133—134°, is readily soluble in benzene, sparingly in alcohol, and yields paranitrodiphenylamine when boiled with potash.

Di-paramidophenylurethane, $(NH_2 \cdot C_6H_4)_2N \cdot COOEt + H_2O$, is prepared by reducing the nitro-compound with tin and hydrochloric acid; it crystallises in violet needles, and melts at 101° with decomposition. When treated with benzoic chloride, it yields a *benzoyl*-derivative, $(NHBz \cdot C_6H_4)_2N \cdot COOEt$, crystallising in flesh-coloured needles and melting at 210°; this is not identical with the substance to which the author had previously and erroneously assigned this formula (Abstr., 1885, 150).

Hexabromodiphenylurethane, $(C_6H_2Br_3)_2N \cdot COOEt$, is obtained by the action of bromine on solutions of diphenylurethane; it crystallises in long, greenish-brown needles, and melts at 184°. When treated with nitric acid, it yields a nitro-compound crystallising in yellowish-brown needles, and melting at about 245° with decomposition. A. J. G.

New Synthesis of Vanillin. By M. Ulrich (*Ber.*, **18**, 2571—2573).—In 1881, Meister, Lucius, and Brüning patented a method for obtaining three isomeric mononitrometamethoxybenzaldehydes. Tiemann (Abstr., 1883, 189) and Schnell (*Ber.*, **17**, 1381) have stated that this method yields not mononitro-, but two dinitro-derivatives; the author, however, finds that when metamethoxybenzaldehyde is nitrated according to the directions of the patent, the three mononitro-derivatives are formed.

The main product of the reaction is *α-nitro-metamethoxybenzaldehyde;* it crystallises in thick, yellow prisms, and melts at 107°. *β-nitrometamethoxybenzaldehyde* is formed in small quantity; it crystallises in needles, and melts at 82—83°. As both these acids give the indigo reaction, they must be the two ortho-nitro-compounds [COH : Me : NO_2 = 1 : 3 : 2 and 1 : 3 : 6]; there is no evidence as to which is which. The third nitro-compound crystallises in cauliflower-like masses interspersed with prisms, melts at 97°, and does not give the indigo reaction; it has the constitution [COH : Me : NO_2 = 1 : 3 : 5].

Paranitromethoxybenzaldehyde, [COH : Me : NO_2 = 1 : 3 : 4], is obtained as follows: methyl metamethoxycinnamate is nitrated at 0° with nitric acid of sp. gr. 1·46, and the paranitro-methyl salt separated by crystallisation from the product, when it is obtained in flat, white needles melting at 163°. The free paranitro-acid prepared from the methyl salt is then oxidised with aqueous potassium permanganate, by which means it is converted into paranitromethoxybenzaldehyde. This crystallises in hair-like needles, melts at 62°, and is soluble in water, alcohol, and benzene. When treated with acetone and soda, it yields a colourless solution from which after a time colourless needles melting at 84° separate. By replacing the nitro-group by hydroxyl, *vanillin* is obtained. A. J. G.

Paramidacetophenone, Orthamidometacetyltoluene, and some of their Derivatives. By J. Klingel (*Ber.*, **18**, 2687—2706).—Paramidacetophenone is best prepared by boiling a mixture of 2 parts aniline, 3 parts zinc chloride, and 5 parts acetic anhydride

for five hours; the product is boiled with hydrochloric acid and treated with sufficient soda solution to precipitate and redissolve the zinc hydroxide. A brown oil then appears, which is separated and distilled with steam to expel aniline. The residue is extracted several times with boiling water, and the united extracts evaporated down; on cooling the amide separates. The yield is 50—60 per cent. of the weight of aniline used. Several salts are described. *Acetylamidacetophenone*, $COMe{\cdot}C_6H_4{\cdot}NHAc$, forms small white needles which melt at 166—167°; it is readily soluble in hot water and in alcohol. *Hydroxyacetophenone*, $COMe{\cdot}C_6H_4{\cdot}OH$ = 1 : 4, is prepared by acting with sodium nitrite on a well-cooled solution of the base in dilute hydrochloric acid, and then slowly heating the product with water until it boils. The phenol is extracted with ether. It forms white needles melting at 107°, readily soluble in hot water, alcohol, and ether. When the aqueous solution is treated with ferric chloride, it acquires a dark-brown colour. *Iodoacetophenone*, $C_6H_4I{\cdot}COMe$, is prepared from the amide by means of the diazo-chloride; it crystallises in white plates which have an agreeable odour and melt at 79°. It dissolves readily in alcohol and ether. When oxidised, it yields pariodobenzoic acid. *Dimethylamidacetophenone*, $COMe{\cdot}C_6H_4{\cdot}NMe_2$, is obtained by the action of methyl iodide on amidacetophenone, and forms yellowish plates melting at 58—59°. It is readily soluble in alcohol, ether, and hot water.

Acetophenoneazonaphthol, $COMe{\cdot}C_6H_4N : N{\cdot}C_{10}H_6{\cdot}OH$, is prepared by the action of the sodium compound of β-naphthol on the diazo-chloride obtained from amidacetophenone. It forms groups of slender, red needles with a slightly green metallic lustre, insoluble in water, sparingly soluble in ether, readily in alcohol. Dilute alkali dissolves it readily, with formation of a dark-red solution.

Orthamidometacetotoluene, [COMe : Me : NH_2 = 5 : 1 : 2], is prepared from toluidine in a manner similar to amidacetophenone as described above. In appearance it is very similar to amidacetophenone; it melts at 102°, and boils at 280—284°. It dissolves readily in hot water, alcohol, ether, and dilute alkali, and is almost insoluble in light petroleum and benzene. Several salts are described; they resemble the salts of amidacetophenone. The *acetyl-derivative* melts at 143—144°; it is readily soluble in warm water and in alcohol.

Acetocresol, $COMe{\cdot}C_7H_6{\cdot}OH$, is prepared similarly to hydroxyacetophenone; it crystallises in reddish prisms melting at 104°, readily soluble in alcohol, ether, and hot water. When treated with ferric chloride, it gives a yellowish-brown coloration.

Dimethylamido-acetotoluene, $COMe{\cdot}C_7H_6{\cdot}NMe_2$, crystallises in groups of flat prisms melting at 95°; it is readily soluble in alcohol, ether, and hot water, almost insoluble in light petroleum.

Acetyliodotoluene, $COMe{\cdot}C_7H_6I$, is prepared by the action of hydriodic acid on the corresponding diazo-chloride; it forms a yellowish crystalline mass melting at 39°, very readily soluble in alcohol and ether, sparingly soluble in light petroleum, benzene, and hot water. When oxidised, it yields *iodophthalic acid*. This crystallises in slender white needles which melt at 203—204°, is very sparingly soluble in boiling water, and dissolves readily in glacial

acetic acid, alcohol, ether, and warm chloroform. The *barium salt* forms slender, white needles very sparingly soluble in boiling water; the *calcium*, *copper*, and *silver* salts were also prepared. When iodophthalic acid is treated with concentrated potash solution, it is partially converted into parahydroxybenzoic acid; nascent hydrogen converts it into benzoic acid. N. H. M.

Mixed Azo-compounds. By E. Bamberger and A. Calman (*Ber.*, **18**, 2563—2567; compare Abstr., 1885, 157).—A mixture of phenylazoacetophenone and ethyl phenylazobenzoylacetate is obtained by mixing aqueous solutions of diazobenzene chloride, ethyl benzoylacetate, and soda.

Phenylazoacetophenone, $COPh\cdot CH_2\cdot N_2\cdot Ph$, is obtained by heating the mixture with alcoholic potash and precipitating with water; it crystallises in slender, golden-yellow needles, melts at 128·5°, and is readily soluble in hot alcohol or acetic acid.

Phenylazobenzoylacetic acid, $COPh\cdot CH(N_2Ph)\cdot COOH$, obtained from the potash salt prepared as above, crystallises in long, citron-yellow needles, melts at 141°, is soluble in ether, alcohol, and acetic acid, and yields phenylazoacetophenone when boiled for some time with dilute soda.

Orthonitrophenylazoacetophenone, $NO_2\cdot C_6H_4\cdot N_2\cdot CH_2\cdot COPh$, crystallising in lustrous, golden-yellow needles melting at 140—141°, and *orthonitrophenylazobenzoylacetic acid*, $NO_2\cdot C_6H_4\cdot N_2\cdot CH(COPh)\cdot COOH$, crystallising in sulphur-yellow needles and melting at 177°, are formed in similar manner from orthonitrodiazobenzene chloride. When heated for some time at the melting point, the acid loses carbonic anhydride, and is converted into the ketone. By the action of hydroxylamine hydrochloride on the ammonium salt, the compound $NO\cdot C_6H_4\cdot N_2\cdot CH(CPh : NOH)\cdot COOH$ is formed; this crystallises in orange-yellow needles, and melts at 142°.

Metanitrotolylparazobenzoylacetic acid,

$$NO_2\cdot C_6H_3Me\cdot N_2\cdot CH(COPh)\cdot COOH,$$

prepared from metanitroparatoluidine, crystallises in silky, golden-yellow needles, melts at 194°, and is very sparingly soluble in cold alcohol or acetic acid. The corresponding *acetophenone*,

$$NO_2\cdot C_6H_3Me\cdot N_2\cdot CH_2\cdot COPh,$$

crystallises in lustrous, citron-yellow needles, melts at 168°, and with hydroxylamine yields the *ketoxime*,

$$NO_2\cdot C_6H_3Me\cdot N_2\cdot CH_2\cdot CPh : NOH;$$

this crystallises in reddish-yellow needles, and melts at 174°.

A. J. G.

Crystallographic Examination of some Organic Compounds. By J. Zingel (*Zeit. Kryst. Min.*, **10**, 414—420).—The crystalline systems and axial ratios are as follows:—Metatrimethamidobenzoic acid chloride, $NMe_3Cl\cdot C_6H_4\cdot COOH$; monosymmetric; $a : b : c = 1{\cdot}9388 : 1 : 0{\cdot}8757$; $\beta = 88°\ 49'$. Metadimethamidobenzoic acid, $NMe_2\cdot C_6H_4\cdot COOH$; asymmetric; $a : c = 1 : 1{\cdot}9403$.

Dinitroparatoluidine (m. p. 69—71°). Rhombic; $a : b : c = 0{\cdot}9965 : 1 : 0{\cdot}5184$. 2, 4-Dinitrophenyl metanitrobenzoate: asymmetric; $a : b : c = 0{\cdot}7137 : 1 : 1{\cdot}7671$. A. J. G.

Phenylacetic Acid. By R. Meyer (*Chem. Centr.*, 1885, 516—518).—Orthoparadinitrophenylacetic acid is prepared by adding phenylacetic acid to concentrated nitric acid and pouring the mixture into concentrated sulphuric acid. The acid crystallises in colourless needles melting at 160° (Abstr., 1884, 178). *Ethyl dinitrophenylacetate* crystallises in colourless needles melting at 35°; it is more stable than the acid.

Paramido-orthonitrophenylacetic acid is formed by reducing the dinitro-compound with ammonium sulphide; it crystallises in long, reddish-yellow needles, which are soluble in alkalis, and also in acids; it melts at 184—186°. Attempts made to convert this compound into orthonitrophenylacetic acid by the diazo-reaction have been without success. *Ethyl amidonitrophenylacetate* crystallises in long, yellow needles melting at 100°; this compound, when treated with an alcoholic solution of ethyl nitrite and hydrochloric acid, yields a compound having the composition $C_{10}H_{10}N_2O_5$, which crystallises in needles melting at 163°. When heated with hydrochloric acid in sealed tubes at 150—160°, this compound is resolved into ethyl chloride, carbonic anhydride, ammonia, and orthonitrobenzoic acid; this owes its production to the formation of *nitrosomethylorthonitrobenzene;* it would, therefore, appear that the compound is *ethyl orthonitrophenylnitrosoacetate*, $NO_2{\cdot}C_6H_4{\cdot}CH(NO){\cdot}COOEt$ [2 : 1].

Nitrosomethylorthonitroparadiazobenzene chloride,

$$NO_2{\cdot}C_6H_3{\cdot}(N_2Cl){\cdot}CH_2NO,$$

is obtained by treating amidonitrophenylacetic acid with hydrochloric acid and amyl or ethyl nitrite. When heated with hydrobromic acid it yields the bromide $NO_2{\cdot}C_7H_5BrNO$, which melts at 151—152°. The chloride boiled with alcohol yields *nitrosomethylorthonitrobenzene*, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NO$ [1 : 2], which, when heated in sealed tubes with hydrochloric acid at 150—160°, is resolved into ammonia and orthonitrobenzoic acid.

Nitrosomethylnitrobenzene, when oxidised by potassium dichromate or permanganate, or ferric sulphate, yields orthonitrobenzaldehyde, melting at 43·5—44·5°. Reduced by ammonium sulphide, it forms *nitrosomethylorthamidobenzene*, $NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NO$, which crystallises in needles melting at 132—133°.

The methyl-derivative of nitrosomethylnitrobenzene,

$$NO_2{\cdot}C_6H_4{\cdot}CHMe{\cdot}NO,$$

melts at 58°; the ethyl compound is an oil. Methylnitrosoamidobenzene, $NH_2{\cdot}C_6H_4{\cdot}CHMe{\cdot}NO$, is an oil volatile in steam; its hydrochloride crystallises in needles melting at 109°.

Orthonitrobenzonitrile, $NO_2{\cdot}C_6H_4{\cdot}CN$ [1 : 2], is formed by heating nitrosomethylnitrobenzene with acetic anhydride and sodium acetate. The nitrosomethylamidobenzene yields, under like conditions, a diacetyl compound, $NHAc{\cdot}C_6H_4{\cdot}CHAc{\cdot}NO$, melting at 127·5—128·5°.

Dinitrophenylacetic acid, reduced by tin and hydrochloric acid, yields amido-oxindole, $NH_2 \cdot C_6H_3 < \begin{matrix} CH_2 \\ NH \end{matrix} > CO$, from which, by the diazo-reaction, the *paradiazonitroso-oxindole chloride*,

$$ClN_2 \cdot C_6H_3 < \begin{matrix} CH(NO) \\ NH \end{matrix} > CO,$$

has been prepared; it crystallises in yellow needles, and when boiled with alcohol yields nitroso-oxindole. P. P. B.

Derivatives of Durene. By J. U. Nef (*Ber.*, **18**, 2801—2807). —*Durylic acid* is best obtained by heating durene with dilute nitric acid (1 vol. acid of sp. gr. 1·4 to 3 vols. water) for three to four hours in a reflux apparatus; the product is allowed to cool, filtered, and the residue extracted with sodium carbonate solution, the unaltered durene being again treated with dilute acid. On adding hydrochloric acid to the alkaline solution, durylic acid is precipitated together with some nitro-compounds, which are removed by treatment with zinc and glacial acetic acid, and distillation in a current of steam. The durylic acid obtained melts at 149°, and agrees in all properties with the acid described by Jannasch (*Zeits. f. Chem.*, **6**, 449), whilst the yield amounts to 15—20 grams from 40 grams durene. *Dinitrodurylic acid* (see also Gissmann, Abstr., 1883, 334) is best prepared by dissolving finely divided durylic acid in pure concentrated sulphuric acid, cooling with ice, and gradually adding a solution of nitre in pure sulphuric acid, with constant stirring. After four or five hours the product is poured upon ice, the nitro-acid filtered off, washed and purified by means of its calcium salt. Its properties have been described by Gissmann (*loc. cit.*). When dinitrodurylic acid is dissolved in a dilute solution of potassium carbonate and potassium permanganate solution gradually added, *dinitropyromellitic acid* is produced. It has a strongly acid odour, is readily soluble even in cold water, extremely so in ether, and crystallises from both solvents in very long, silky, colourless needles; soluble also in alcohol and glacial acetic acid, but insoluble in chloroform, benzene, and light petroleum. When it is heated in a capillary tube, it loses water (100—160°), and becomes yellow, and it decomposes at 203° with evolution of gas. The silver salt, $C_6(NO_2)_2(COOAg)_4$, forms a golden-yellow, amorphous precipitate. Attempts to reduce dinitropyromellitic acid to the diamido-acid proved unsuccessful. *Ethyl dinitropyromellitate*, $C_6(NO_2)_2(COOEt)_4$, obtained by heating the silver salt with ethyl iodide and ether for one to two hours at 100°, forms magnificent, colourless needles, readily soluble in hot, and sparingly in cold alcohol, readily in benzene, chloroform, glacial acetic acid, acetone, and ethyl acetate, more sparingly in ether. It melts at 130°. When its hot solution in glacial acetic acid is treated with zinc-dust, *ethyl azopyromellitate*, $C_6N_2(COOEt)_4$, is produced. This has a deep cinnabar-red colour, is insoluble in water and dilute acids; it yields a colourless salt with concentrated hydrochloric acid, dissolves readily in glacial acetic acid, alcohol, and ether, and melts at 134°. It sublimes without decomposition when heated. When

diamidodurene (from dinitrodurene) is treated with ferric chloride, a green coloration is produced, and at once changes to yellow, owing to the formation of *duroquinone*, $C_6O_2Me_4$. This crystallises from light petroleum in long, yellow needles melting at 111°. It sublimes readily, emitting but a faint quinone odour, dissolves very readily in ether, chloroform, benzene, alcohol, and acetone. Zinc-dust and soda solution, sulphurous acid, and sodium amalgam reduce it, but it is reproduced on agitation with air. It is insoluble in alkalis, and nearly so in hot water. Potassium permanganate and sodium carbonate solution, and also chromic acid and glacial acetic acid, decompose it.

From the great stability of duroquinone, the author hopes to succeed in preparing the quinone of pyromellitic acid, which would have the same composition as croconic acid. A. K. M.

Dibromoparahydroxybenzoic Acid. By A. Alessi (*Gazzetta*, **15**, 242—247).—In order to determine the constitution of the dibromoparahydroxybenzoic acid obtained by Balbiano from the distillation of sodium dibromanisate with calcium oxide (Abstr., 1884, 1172), dibromanisic acid was converted by excess of concentrated hydriodic acid into a dibromohydroxybenzoic acid. This was found to be identical with Balbiano's acid. As in the acid from dibromanisic acid, the substituted groupings must be in the relative position OMe : Br : Br : $CO_2H = 1 : 2 : 6$, the composition of Balbiano's acid has the same constitution. V. H. V.

Salts of Anisic Acid. By G. Borrella (*Gazzetta*, **15**, 304—305).—The copper, manganese, nickel, cobalt, zinc, and cadmium salts of anisic acid, crystallise with H_2O; there can also be obtained basic copper, $OMe{\cdot}C_6H_4{\cdot}COOCuOH$, and chromium,

$$[(OMe.C_6H_4{\cdot}COO)_6Cr_2]_2,Cr_2(OH)_6,$$

salts. In analysing the metallic salts of the organic acids, it is convenient to precipitate the heavy metals in the form of oxalates, the alcohol necessary for the complete precipitation serving to dissolve the liberated acid. V. H. V.

Inner Condensations. By A. Rössing (*Chem. Centr.*, 1885, 593—595).—*Ortho-aldehydophenoxyacetic acid*, $COH{\cdot}C_6H_4{\cdot}OCH_2{\cdot}COOH$, produced by the action of monochloracetic acid on salicylaldehyde, crystallises in large, yellow leaflets, melting at 132°. Its salts with the alkali metals and metals of the alkaline earths are soluble in water, its copper and silver salts sparingly soluble in water. It reduces ammoniacal solutions of silver salts, and forms a double compound with hydrogen sodium sulphite. Its *ethyl* salt melts at 114°. It unites directly with aniline, forming the compound

$$NHPh{\cdot}CH(OH){\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}COOH.$$

This compound unites with acids, forming well-defined salts, from which the base can be obtained by careful addition of ammonia or caustic alkalis, or better still by decomposition with an alcoholic solution of sodium ethoxide.

Aldehydophenoxyacetic acid unites directly with phenylhydrazine, forming the compound $N_2HPh : CH\cdot C_6H_4\cdot O\cdot CH_2\cdot COOH$, which melts at 105°. By oxidising agents, aldehydophenoxyacetic acid is converted into *salicyloxyacetic acid*, $COOH\cdot C_6H_4\cdot O\cdot CH_2\cdot COOH$, which crystallises in white needles, melting at 186—187°. *Ethyl salicyloxyacetate* is a light yellow oil, which decomposes when heated, and is converted into the corresponding diamide,

$$NH_2\cdot CO\cdot C_6H_4\cdot O\cdot CH_2\cdot CONH_2;$$

when heated in sealed tubes with ammonia; this crystallises in yellow needles melting at 158°.

When aldehydo-phenoxyacetic acid is heated with acetic oxide and sodium acetate, it yields *orthocumaroxyacetic acid*,

$$COOH\cdot CH : CH\cdot C_6H_4\cdot O\cdot CH_2\cdot COOH,$$

which crystallises from water in needles melting at 190°. This compound, like cinnamic acid, combines with bromine to form a dibromide, melting at 219—220°, which when heated with alcoholic potash, yields *orthopropiolphenoxyacetic acid*,

$$COOH\cdot C : C\cdot C_6H_4\cdot O\cdot CH_2\cdot COOH;$$

this forms small yellow crystals melting at 208°.

When aldehydo-phenoxyacetic acid is heated with five parts of acetic oxide and 4—5 parts of sodium acetate, for three hours, it yields an oil boiling at 170°, which is identical with cumarone, $C_6H_4<\begin{matrix}CH\\ -O\end{matrix}>CH$ (Abstr., 1883, 474). If orthocumaroxyacetic acid is heated with phosphoric acid, it loses water and yields the anhydride

$$C_6H_4<\begin{matrix}CH : CH\cdot CO\\ -O\cdot CH_2\cdot CO-\end{matrix}>O,$$

which melts at 176°; when boiled with water, it is easily reconverted into the acid. This anhydride unites directly with bromine, forming the dibromide $C_6H_4<\begin{matrix}CHBr\cdot CHBr\\ O\cdot CH_2\cdot CO\cdot O\end{matrix}>CO$, crystallising in yellow needles melting at 213°.

When the compound of aldehydo-phenoxyacetic acid and phenylhydrazine is heated with sulphuric acid, a bluish-green amorphous substance is produced, which dissolves in alcohol, forming a bluish-green solution, and in alkalis, forming cherry-red solutions. This compound is precipitated from its alcoholic solutions by ether, as a lustrous black powder, having the composition $C_9H_7NO_3$, and melting at 108°. This same compound can be prepared by heating a mixture of monochloracetic acid with ortho-oxybenzylidene phenylhydrazine in sealed tubes at 100°. Orthoxybenzylidene phenylhydrazine when heated with acetic oxide yields a diacetic derivative $AcO\cdot C_6H_4\cdot CH : N_2AcPh$, which crystallises in needles or prisms melting at 133°. On dry distillation, this compound yields acetanilide and a reddish-yellow substance containing nitrogen. The diacetyl-derivative forms a dibromide which is easily decomposed, and when boiled with alcohol yields *acetoxydibromobenzylidenephenylhydrazine*,

$AcO{\cdot}C_6H_2Br_2{\cdot}CH : N_2HPh$, melting at 188°; this is decomposed by boiling with caustic soda; from the alkaline solution, hydrochloric acid precipitates the compound $HO{\cdot}C_6H_2Br_2{\cdot}CH : N_2HPh$, melting at 148°. P. P. B.

Constitution of the Phthalic Acids. By E. Nölting (*Ber.*, **18**, 2687).—The constitution of the phthalic acids has long been known, but the proofs are of a complex nature. The author now advances a simple proof. The three xylenes when oxidised readily yield the three phthalic acids. Three isomeric nitroxylenes, xylidines, and xylenols are derived from metaxylene, two from orthoxylene, one only from paraxylene. Therefore the carboxyl-groups must occupy the 1 : 3 positions in isophthalic acid, the 1 : 2 positions in phthalic acid, and the 1 : 4 positions in terephthalic acid. A. J. G.

Nitration of Phenylparaconic Acid. By H. Erdmann (*Ber.*, **18**, 2741—2743).—Paranitrophenylparaconic acid is prepared by the nitration of phenylparaconic acid. It forms very bright yellow plates which melt at 155°. It is insoluble in carbon bisulphide and dissolves sparingly in chloroform, benzene, and ether, readily in alcohol, glacial acetic acid, hot xylene, &c. When heated at 200°, evolution of carbonic anhydride takes place. Potassium permanganate converts it into paranitrobenzoic acid.

In the preparation of this acid, the ortho-acid is also formed (compare Abstr., 1885, 1224). N. H. M.

Derivatives of Durene. By O. Jacobsen and E. Schnapauff (*Ber.*, **18**, 2841—2844).—When powdered durene is gradually added to about $2\frac{1}{2}$ times its weight of cooled sulphuric monochloride, durenesulphonic chloride is obtained as the chief product, together with durylsulphone and a little durenesulphonic chloride. On treating the product with ice and water, the sulphuric, hydrochloric, and sulphonic acids are separated from the sulphonic chloride and the sulphone, and on adding an excess of soda to the acid filtrate, the sodium sulphonate separates out. The sulphonic chloride may be separated from the sulphone by crystallisation from alcohol, and finally from ether. *Durenesulphonic acid*, $C_{10}H_{13}{\cdot}SO_3H$, dissolves readily in water, but only sparingly in moderately dilute sulphuric acid; the sodium, potassium, barium, and copper salts are described.

Durenesulphonic chloride, $C_{10}H_{13}{\cdot}SO_2Cl$, crystallises from warm ether in brittle prisms of vitreous lustre, melts at 99°, dissolves readily in warm, sparingly in ice-cold alcohol, and very readily in ether. *Durenesulphonamide*, $C_{10}H_{13}{\cdot}SO_2NH_2$, crystallises from alcohol in long prisms melting at 155°; it is very readily soluble in hot, sparingly in cold alcohol and in ether, and is almost insoluble in cold water; it is decomposed by concentrated hydrochloric acid at 190°.

Durylsulphone, $(C_{10}H_{13})_2SO_2$, is readily soluble in alcohol, ether, benzene, and light petroleum, whilst boiling water dissolves but traces. It crystallises in long prisms melting at 37°. It can be distilled under diminished pressure without decomposition, but at the

atmospheric pressure it yields sulphurous acid and durene. When heated with concentrated hydrochloric acid at 200°, it splits up into durene and sulphuric acid.

When sodium durenesulphonate is fused with potash, either durenol or hydroxydurylic acid is produced, accordingly to the temperature and time of heating. *Durenol*, $C_{10}H_{13}\cdot OH$, crystallises from warm alcohol in large, flat prisms, melts at 117°, and boils at 249—250°. *Bromodurenol*, $C_{10}H_{12}Br\cdot OH$, crystallises from hot dilute alcohol in long, vitreous prisms, melting at 118°. It is readily soluble in alcohol and ether, insoluble in water. *Nitrodurenol*, $C_{10}H_{12}(NO_2)\cdot OH$, separates from hot dilute alcohol as a bright yellow mass. It melts at 130°, is almost insoluble in water, very readily soluble in alcohol, and also in alkalis and alkaline carbonates with dark yellow coloration.

Hydroxydurylic acid, $C_6HMe_3(OH)\cdot COOH$, is almost insoluble in cold, sparingly soluble in hot water, but very readily in alcohol. Its constitution is [COOH : OH : Me_3 = 1 : 2 : 3 : 4 : 6]. It crystallises in small needles, melts at 148°, and may be sublimed without decomposition. Its salts give a dirty brown precipitate with ferric chloride, whilst a solution of the free acid in dilute alcohol gives a transient blue coloration. The calcium salt, $(C_{10}H_{11}O_3)_2Ca + 2H_2O$, is described. When the acid is heated at 190—200° with hydrochloric acid, carbonic anhydride and pseudocumenol (melting at 85—88°) are produced. A. K. M.

Phenylacridine. By A. Claus and C. Nicolaysen (*Ber.*, **18**, 2706—2712).—Potassium permanganate acts on phenylacridine in presence of free sulphuric acid with formation of a mixture of paraphenylquinolinecarboxylic acids, from which a di- and a monocarboxylic acid were separated. *Paraphenylquinolinedicarboxylic acid*, $Ph\cdot C_9NH_4(COOH)_2$, forms lustrous needles melting at 200—215°. The *barium salt* (with 4 mols. H_2O) crystallises in slender, colourless needles. *Barium paraphenylquinolinecarboxylate*, $(C_{16}H_{10}NO_2)_2Ba,6H_2O$, crystallises in needles.

Phenylamidobenzoic acid, $NHPh\cdot C_6H_4\cdot COOH$, is obtained by the oxidation of phenylacridine methyl chloride with potassium permanganate. It forms small colourless needles melting at 222° (uncorr.), almost insoluble in water, readily soluble in ether, chloroform, &c. The *sodium salt* (with 4 mols. H_2O) forms colourless plates readily soluble in water; the *barium* (with 5 mols. H_2O) and *silver* salts are also described.

An acid having all the properties of that just described, is obtained by heating metamidobenzoic acid with aniline hydrochloride at 220°.

Phenylacridine hydrochloride crystallises from pure water in red octahedra (with 5 mols. H_2O); the long, yellow, anhydrous needles described by Bernthsen are obtained from a solution containing free hydrochloric acid. N. H. M.

α-Naphthylaminephthaleïn. By A. Vanni (*Gazzetta*, **15**, 346—347).—On heating phthalic anhydride and α-naphthylamine in equal molecular proportions at a temperature of 150°, a fused mass is

formed; this is heated with boiling alcohol, and the filtered solution as it cools deposits α-naphthylaminephthaleïn,

$$C(NH\cdot C_{10}H_7)_2<\begin{matrix}C_6H_4\\-O-\end{matrix}>CO,$$

in the form of colourless, transparent, prismatic tables. It is insoluble in water, sparingly soluble in alcohol and ether, and melts at 166°. It is decomposed by concentrated sulphuric acid, forming a pale yellow substance, which dissolves in ammonia with an orange-red coloration; with concentrated potash, it forms an oil which ultimately solidifies; the compound formed gives a violet coloration with water.

V. H. V.

Relations of α- to β-Hydrojuglone. By F. Mylius (*Ber.*, **18**, 2567—2571).—The acetyl- or benzoyl-derivatives prepared from α- and from β-hydrojuglone are identical, and seem to be the β-derivatives, inasmuch as they yield β-hydrojuglone when treated with alkalis or sulphuric acid. The compound previously described as triacetyl-α-hydrojuglone (Abstr., 1885, 170) should therefore be termed *triacetyl-β-hydrojuglone*. It crystallises in colourless prisms, and melts at 129—130°. *Tribenzoyl-β-hydrojuglone*, $C_{10}H_5O_3Bz_3$, crystallises in colourless needles, melts at 228—229°, and like the acetyl-derivative, can be sublimed unchanged.

α-Hydrojuglone when heated above its melting point in an atmosphere of hydrogen is converted into β-hydrojuglone, which distils; on the other hand, when the β-compound is subjected to prolonged boiling with dilute hydrochloric acid, it is converted into α-hydrojuglone.

A. J. G.

Action of Ammonia on Anthragallol. By S. v. Georgievics (*Monatsh. Chem.*, **6**, 754—759).—*Anthragallolamide*,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H(OH)_2NH_2\ [NH_2:(OH)_2=1:2:3?],$$

is prepared by boiling anthragallol with excess of ammonia for 20—30 minutes; the fine blue solution so obtained is evaporated down, and the solid substance crystallised from alcohol or glacial acetic acid. It forms greenish-black needles or a reddish-brown, crystalline powder, sparingly soluble in hot water, alcohol, and benzene, &c. Alkalis and sulphuric acid dissolve it unchanged, with formation of blue and intense red solutions respectively. Nitrous acid acts on it with formation of a yellow substance which melts at 190—200°; it does not contain nitrogen, and is probably dihydroxyanthragallol $[(OH)_2=2:3]$.

Two *nitro*-derivatives of anthragallol were obtained from gallic acid by the action of meta- and of para-nitrobenzoic acid.

Anthragallolsulphonic acid is prepared by heating anthragallol with 3—4 times its weight of sulphuric acid at 130—140°. The aqueous solution acquires a red colour when treated with the smallest trace of alkali. The *sodium* and *potassium* salts have colouring properties.

N. H. M.

Terpenes and Ethereal Oils. By O. Wallach (III) (*Annalen*, **230**, 225—272).—Pure borneol, prepared by the action of sodium on camphor, melts at 206—207°, not at 198° as generally stated. This compound behaves like a saturated secondary alcohol, but it has the property of uniting with bromine and hydrogen bromide, &c., to form unstable additive products. For example, when bromine is added to a solution of borneol in light petroleum, a crystalline precipitate is deposited, which consists chiefly of *borneol bromide*, $C_{10}H_{18}O{\cdot}Br_2$, mixed with a small quantity of $(C_{10}H_{18}O)_2Br_2$. Cineol, like borneol, unites with bromine in two different proportions, forming compounds which have the same composition as the borneol bromides. When borneol bromide is covered with light petroleum and left for some time in a closed vessel, decomposition ensues resulting in the formation of borneol and borneol hydrobromide, $(C_{10}H_{18}O)_2,HBr$. The same compound is obtained as a white, crystalline powder by the action of hydrogen bromide on a solution of borneol in light petroleum. It is decomposed by water and alcohol.

The *hydriodide*, $(C_{10}H_{18}O)_2,HI$, is a white, crystalline compound, which decomposes spontaneously.

Bornyl chloride, $C_{10}H_{17}Cl$, is easily prepared by adding borneol to a mixture of phosphorus pentachloride and light petroleum. The action is finished in half an hour. The crude product is poured into water, and repeatedly washed. Bornyl chloride is not identical with pinene hydrochloride. It is readily converted into camphene by heating with aniline. Camphene is decomposed by dehydrating agents, such as zinc chloride and strong sulphuric acid, or by the action of heat alone. In each case the decomposition products are liquid. Monobromocamphene is obtained as an oily liquid when bromine is added to a solution of camphene in alcohol and ether.

Camphene is formed by the action of dehydrating agents on borneol, but the hydrocarbon cannot be isolated (except when potassium pyrosulphate is the dehydrating agent) as it is decomposed by zinc chloride or phosphoric anhydride or strong sulphuric acid.

The so-called hydrocarbon "*borneen*," which Pelouze (*Annalen*, **40**, 327), Kachler (*ibid.*, **164**, 78), and Oppenheim (this Journal, 1874, 891) obtained by the action of phosphoric anhydride on borneol, is a mixture of the decomposition products of camphene.

The author confirms Tilden's statement (Trans., 1878, 80 and 251), that Russian and Swedish oil of turpentine contain the same constituents, namely, australene, sylvestrene, and dipentene. The hydrocarbon obtained by decomposing sylvestrene chloride with aniline closely resembles sylvestrene, but the identity of the bodies is not proved. The hydrocarbons yield a chloride melting at 72°, and a liquid bromide.

"*Terpinol*" described by Wiggers (*Annalen*, **57**, 252), and by List (*ibid.*, **67**, 367), does not exist.

Terpine hydrate, $C_{10}H_{20}O_2 + H_2O$, melts at 117°. It is a saturated compound, and is decomposed by boiling with acids or dehydrating agents, yielding terpineol, $C_{10}H_{18}O$, and other products. When a mixture of 1 part of sulphuric acid and 2 of water is used, terpineol, terpinene, $C_{10}H_{16}$, and terpinolene are formed. When very

dilute sulphuric acid is used, the chief product is terpinene. Dilute phosphoric acid and glacial acetic acid on the other hand yield terpineol as the principal product. Terpine hydrate is almost completely converted into dipentene by prolonged treatment with potassium pyrosulphate.

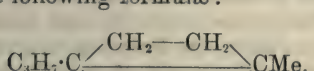
Terpineol, $C_{10}H_{17}\cdot OH$, is a nonsaturated monatomic alcohol. It is a thick liquid, boiling at 215°, and is sparingly soluble in water. It unites with bromine to form an unstable bromide.

Dipentene tetrabromide, melting at 124°, is formed by the action of an excess of bromine on terpineol. The hydroxyl in terpineol is easily replaced by chlorine or iodine, yielding for example the chloride, $C_{10}H_{18}Cl_2$, melting at 50°, and the iodide melting at 77°. Terpineol unites with carbanil, forming phenylterpinylurethane, which crystallises in white needles melting at 110°. Boiling with dilute acids, or treatment with dehydrating agents, converts terpineol into terpene or dipentene, but if terpineol is left at the ordinary temperature in contact with dilute sulphuric or hydrochloric acid, it unites with water, forming terpine hydrate, $C_{10}H_{20}O_2 + H_2O$.

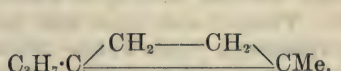
Terpine has the same boiling point as dipentene, but the two compounds are not identical, as the former yields a liquid bromine-derivative. Terpine is formed by the inversion of pinene with alcoholic sulphuric acid.

Terpinolene has not yet been obtained in a pure state. It boils between 185° and 190°, and yields an unstable tetrabromide crystallising in monoclinic plates.

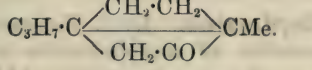
The relation between camphene, borneol, and camphor is shown by the following formulæ:—



Camphene.



Borneol.



Camphor.

Borneol bears the same relation to camphene that terpineol does to dipentene. W. C. W.

Action of Picric Acid on Terebenthene. By — Lextreit (*J. Pharm.* [5], **11**, 211—213).—Terebenthene, when heated with picric acid at 150°, gives a limpid liquid, which, after further heating at the same temperature, deposits crystals on cooling. When freed from excess of picric acid and a brown colouring matter, it forms thin, friable, transparent flakes, which rapidly take a yellow tint when exposed to light. It is insoluble in water, slightly soluble in cold alcohol, readily in ether, carbon bisulphide, and boiling alcohol. When heated, it first fuses, and then decomposes with a gentle deflagration. It seems to be a compound of picric acid and camphene of the formula $C_{10}H_{16},C_6H_3(NO_2)_3O$. It is more stable towards aqueous

alkalis than are the known picrates of hydrocarbons. Further, with an alcoholic solution of potash a very explosive, crystalline precipitate of a purplish-red colour is formed quite different from potassium picrate. The compound is rapidly decomposed by a boiling aqueous solution of soda; a white sublimate is carried over with the steam, which is insoluble in water, but soluble in almost all proportions in cold alcohol and ether. Its odour resembles both that of camphor and of camphene. It fuses at 179°, camphor at 175°, and camphene at 45°. Its rotative power is $\alpha_D = -36°$. Its composition is very nearly the same as that of camphor. Picric acid behaves similarly with thymol.

J. T.

Natural Camphor Oils. By P. MacEwan (*Pharm. J. Trans.* [3], **15**, 1045—1046).—Borneo, Formosa, and Japanese oils are referred to. The Bornean oil, sp. gr. about 0·900, consists chiefly of borneene with a small quantity of resinous matter, but with no camphor (borneol) in solution. In contact with copper, it acquires a green colour in a day or two. The Formosa camphor oil, sp. gr. 0·943, is a saturated oleaceous solution of camphor; when rubbed on the hand, there is at first a strong camphoraceous odour, which soon goes off, and a sassafras-like odour remains, but the oil dries quickly on the skin and leaves no mark. Japanese camphor oil in crude form, according to Oishi (Abstr., 1885, 270), has sp. gr. 0·959, and contains camphor. The sample examined by the author, evidently purified, of sp. gr. 0·951, had a strong sassafras-like odour, and contained no camphor. Scarcely any of it distilled below 140°, about 10—12 per cent. consisting of a liquid isomeride of camphor, distilled between 180° and 185°, nearly one-half distilled over up to about 205°; the residue has a sp. gr. of 0·995. Treated with nitric acid and then after a minute with water, the Japanese oil yields a clear crimson solution, the Formosa oil a very slightly green, milky solution; with hydrochloric acid, they both yield salmon-coloured solutions. This oil is used in the United States to adulterate oil of wintergreen.

D. A. L.

Camphophenylhydrazine. By L. Balbiano (*Gazzetta*, **15**, 246—248).—As the formation of camphoroxime seems to indicate the presence of the carbonyl-group in camphor (Abstr., 1883, 728; 1884, 610), although the evidence thus far is not sufficient to decide between the aldehydic and ketonic groups, the author has studied the reaction between phenylhydrazine hydrochloride and camphor in the presence of sodium acetate. In this way camphophenylhydrazine, $C_{10}H_{16}{\cdot}N_2HPh$, is produced. It is a yellowish oil, distilling at 235—245° under a pressure of 170 mm., soluble in dry ether, and decomposed by hydrogen chloride to form phenylhydrazine hydrochloride.

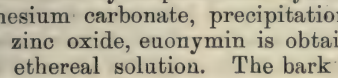
Borneo camphor does not react with hydroxlamine under the same conditions in which camphor yields camphoroxime; whilst by treatment with phenylhydrazine in the presence of diluents, bromocamphor yields phenylhydrazine hydrobromide and resinous substances.

V. H. V.

Euonymin. By G. Romm (*Chem. Centr.*, 1885, 442—443).—This glucoside is not to be confounded with the medical preparation of the same name, as the latter contains no poison, and is employed as an

aperient. The author prepares it by extracting the powdered rinds of *Euyonmus atropurpureus* with 70 per cent. alcohol, distilling and evaporating the extract, diluting with water and filtering; the filtrate is then precipitated by lead acetate, again filtered, and the clear liquor freed from lead by sulphuretted hydrogen. After neutralisation with magnesium carbonate, precipitation with tannic acid, and treatment with zinc oxide, euonymin is obtained in crystals on evaporation of its ethereal solution. The bark of *Euonymus europæus* contains no euonymin. J. K. C.

Constitution of Santonin. By S. Cannizzaro (*Ber.*, **18**, 2746—2751).—After reviewing the evidence at present available as to the constitution of santonin, the author suggests the formula—



as agreeing fairly with its reactions.

Derivatives of Santonin. By V. Villavecchia (*Ber.*, **18**, 2859—2864).—*Photosantonic acid*, $C_{15}H_{22}O_5$, is best obtained by exposing a solution of 10 grams santonin in a litre of acetic acid (sp. gr. 1·06) to the action of light for about a month; the product is evaporated to a syrupy consistence in a vacuum, the residue washed with water, and then treated with a warm solution of sodium carbonate. The undissolved residue may be dissolved in alcohol, from which it crystallises in prisms, melting at 182—183°, and of the composition $C_{17}H_{22}O_5$, namely, 1 mol. santonin + 1 mol. acetic acid. On adding hydrochloric acid to the sodium carbonate extract, photosantonic acid separates, and is purified by repeated crystallisation from alcohol. Its properties agree with those assigned to it by Sestini (Abstr., 1877, 471). It loses 1 mol. H_2O at 100°, and melts at 154—155°. The composition of its salts indicates that the water lost at 100° is not water of crystallisation as assumed by Sestini, but that undried photosantonic acid bears the same relation to the dried acid, as santonin does to santonic acid. Barium and silver photosantonates, $C_{15}H_{20}O_5Ba$ and $C_{15}H_{20}O_5Ag_2$, are described.

Photosantonin, $C_{17}H_{24}O_4$, is best prepared by exposing a solution of santonin (20 grams) in alcohol (1 litre) to the direct action of light for three months. The alcohol is distilled off in a vacuum, and the thick residual oil treated with lukewarm sodium carbonate solution to remove photosantonic acid. On treating the insoluble portion with ether, two isomeric photosantonins, $C_{17}H_{24}O_4$, are obtained; one modification forms platy crystals, melting at 154—155°, and is dextrorotatory; $[\alpha]_D = +76{\cdot}77°$ for a solution containing 0·3825 gram in 50 c.c. alcohol at 13°. The other modification, which is the chief product, melts at 68—69°, and is identical with Sestini's photosantonin. It is readily soluble in alcohol and ether, and almost insoluble in cold water; $[\alpha]_D = -121{\cdot}6°$ for a solution containing 1·0010 gram in 50 c.c. alcohol at 14°, and $-118{\cdot}4°$ for 1·0980 gram in 50 c.c. alcohol also at 14°. The composition of photosantonin shows that it is not the diethyl salt of photosantonic acid as

Sestini assumed, but the monethyl-derivative of dehydrated photosantonic acid, which is regarded as a lactonic acid, thus:—Photosantonic acid, $HO{\cdot}C_{13}H_{19}(COOH)_2$; photosantonic acid dried at 100°, $COOH{\cdot}C_{13}H_{19}<^{-O-}_{CO}>$; photosantonin, $COOEt{\cdot}C_{13}H_{19}<^{-O-}_{CO}>$. The last compound may also be obtained from photosantonic acid, alcohol, and sulphuric acid, and by the action of ethyl iodide on the silver salt.

When gaseous hydrogen chloride is passed into a solution of photosantonic acid in absolute alcohol, the diethyl-derivative of an acid containing the elements of a molecule of water less than photosantonic acid is obtained; it is termed *ethyl dehydrophotosantonate*, $C_{13}H_{18}(COOEt)_2$, and forms a colourless liquid, which does not solidify at − 10°. A solution of 0·7306 gram in 25 c.c. alcohol has a dextrorotatory power at 20·4°, $[\alpha]_D = + 20{\cdot}4°$. The free acid which is isomeric with dehydrated photosantonic acid, melts at 132—133°. It is very readily soluble in alcohol and ether; its dextrorotatory power is $[\alpha]_D = + 31{\cdot}9°$ for a solution containing 0·7114 gram in 50 c.c. alcohol. The barium salt, $C_{15}H_{18}O_4Ba$, is very readily soluble.

A. K. M.

Papain. By S. H. C. Martin (*Pharm. J. Trans.* [3], **15**, 129—130).—A glycerol extract of commercial papain retains the fermentative activity of the powder, and contains a hemialbumose in quantity, together with a mere trace of globulin. When the latter is precipitated by magnesium sulphate, and the hemialbumose by subsequent saturation with sodium sulphate, the solution is no longer active. The aqueous solution of the precipitated hemialbumose is, however, very active, and when tested on coagulated egg-albumin produced peptones; it is therefore evident that the ferment of papaw-juice is associated with the hemialbumose, but as yet has not been separated from it. Papain acts on animal albumin in manner similar to pepsin, but not so rapidly; with milk it behaves like pancreatic juice, first curdling it, the curdling being intensified by raising the temperature (but not above 62°), and hindered by making the milk alkaline, or by diluting it to some extent, or by boiling previous to adding cold water; the curd is gradually dissolved with the production of peptones, leucine, and tyrosine. A hemialbumose is formed as an intermediate product between the caseïn and peptones.

With regard to the action of papain on the proteïds of papaw-juice, it converts the globulins into an albumose corresponding with Vine's hemialbumose; leucine and tyrosine being also formed, but no true peptones have been detected.

D. A. L.

Pyrrylene Dimethyl Ketone. By G. Ciamician and P. Silber (*Gazzetta*, **15**, 248—250).—In this paper it is shown that pyrrylene dimethyl ketone (dipseudacetopyrroline) is producible not only from pseudacetopyrroline and acetic anhydride, as indicated formerly (Abstr., 1885, 378), but also directly from pyrroline by means of the same reaction. By an excess of fuming nitric acid, it is converted into a mono-nitro-derivative, $C_4NH_2(NO_2)Ac_2$, melting at 149°, and possessing acid properties.

V. H. V.

Synthesis of Pyrroline-derivatives. By L. Lederer and C. Paal (*Ber.*, **18**, 2591—2599).—It has been already shown that pyrroline derivatives are formed by the action of ammonia on acetophenoneacetone and on acetonylacetone (Abstr., 1885, 516, 1206), and of ammonia and primary amines on ethyl acetosuccinate (Knorr, *ibid.*, 554, 994), the reaction is now extended to ethyl acetophenoneacetoacetate.

Ethylic methylphenylpyrrolinecarboxylate, $C_4NH_2MePh{\cdot}COOEt$ [Me : COOEt : Ph = 2 : 3 : 5], is obtained by allowing a mixture of ethyl acetophenoneacetate and aqueous ammonia to remain for 24 hours; it crystallises in colourless tables or small needles, and melts at 120°. *Methylphenylpyrrolinecarboxylic acid*,

$$C_4NH_2MePh{\cdot}COOH,$$

prepared from the ethyl salt by saponification, &c., crystallises in long, flat, yellowish needles, readily soluble in acetic acid, benzene, and hot alcohol. When heated, it partially decomposes at 175°, and melts at 190°; it sublimes in small part, but does not yield methylphenylpyrroline.

Ethylic dimethylphenylpyrrolinecarboxylate, $C_4NHMe_2Ph{\cdot}COOEt$ [Me : Me : COOEt : Ph = 1 : 2 : 3 : 5], prepared in manner similar with methylamine, crystallises in colourless plates, softens at 90°, melts at 112°, and is readily soluble in alcohol, ether, and benzene.

Methylphenylallylpyrrolinecarboxylic acid, $C_3H_5{\cdot}C_4NHMePh{\cdot}COOH$ [C_3H_5 : Me : Ph : COOH = 1 : 2 : 3 : 5]. The *ethyl* salt is prepared by heating ethyl acetophenoneacetoacetate with allylamine and a little absolute alcohol in sealed tubes at 130° for an hour; it is a thick oil, and does not crystallise. The free acid crystallises in short, lustrous prisms, is readily soluble in alcohol, ether, benzene, and acetic acid, and melts at 158°. *Methylphenylallylpyrroline*, $C_3H_5{\cdot}C_4NHMePh$ [1 : 2 : 5], is prepared by distilling the acid; it crystallises in large plates, melts at 52° to a colourless oil with blue fluorescence, boils at 277—278°, and is soluble in all proportions in ether, alcohol, benzene, light petroleum, and acetic acid.

Methyldiphenylpyrrolinecarboxylic acid,

$$C_4NHMePh_2{\cdot}COOH\ [Ph : Me : COOH : Ph = 1 : 2 : 3 : 5],$$

crystallises in small needles, melts at 226°, and is readily soluble in acetic acid and benzene. The *ethyl* salt, $C_4NHMePh_2{\cdot}COOEt$, is prepared by boiling ethyl acetophenoneacetoacetate (1 part) with aniline (1·5 part) dissolved in acetic acid; it crystallises in small prisms, melts at 100°, and is sparingly soluble in alcohol and acetic acid. *Methyldiphenylpyrroline*, $C_4NH_2MePh_2$, is prepared by heating the free acid at above 226°; it crystallises in large, colourless tables, melts at 84°, is not very readily volatile with steam, and is readily soluble in benzene and light petroleum.

Methylphenylorthotolylpyrrolinecarboxylic acid,

$$C_6H_4Me{\cdot}C_4NHMePh{\cdot}COOH,$$

crystallises in small prisms, and melts at 199°; it is readily soluble in the ordinary solvents except water. The *ethyl* salt is obtained by boil-

ing aniline, acetic acid, and orthotoluidine, as a thick oil that cannot be crystallised. *Methylphenylorthotolylpyrroline*,

$$C_6H_4Me{\cdot}C_4NH_2MePh\ [1:2:5],$$

is obtained by the dry distillation of the free acid; it crystallises in plates, melts at 44° to a pale-yellow, fluorescent oil, boils at 325—328°, and is readily soluble in alcohol, ether, benzene, and light petroleum.

Methylphenylparatolylcarboxylic acid, $C_6H_4Me{\cdot}C_4NHMePh{\cdot}COOH$, resembles benzoic acid in appearance, and melts at 227°. The *ethyl* salt, $C_{21}H_{21}NO_2$, crystallises in prisms or tables, and melts at 115°. *Methylphenylparatolylpyrroline*, $C_6H_4Me{\cdot}C_4NH_2MePh$, crystallises in concentric groups of slender needles or in tables, melts at 91°, boils above 350°, and is readily soluble in light petroleum and benzene.

Methylphenyl-α-naphthylpyrrolinecarboxylic acid,

$$C_{10}H_7{\cdot}C_4NHMePh{\cdot}COOH\ [C_{10}H_7:Me:COOH:Ph=1:2:3:5],$$

is prepared by heating α-naphthylamine and ethyl acetophenoneacetate in sealed tubes at 130°, and saponifying the uncrystallisable product. It crystallises in needles, melts at 244°, and is readily soluble in alcohol, benzene, and acetic acid. *Methylphenyl-α-naphthylpyrroline*, $C_{10}H_7{\cdot}C_4NH_2MePh$, crystallises in plates, melts at 74°, boils above 360°, and is very readily soluble in benzene, light petroleum, and alcohol.

Methylphenyl-β-naphthylpyrroline, $C_{10}H_7{\cdot}C_4NH_2MePh$, crystallises in concentrically grouped needles, and melts at 52°. The *carboxylic acid*, $C_{10}H_7{\cdot}C_4NHMePh{\cdot}COOH$, crystallises in small, white needles, and melts at 249°. Its *ethyl* salt, $C_{24}H_{21}NO_2$, crystallises in lustrous plates, and melts at 115°. A. J. G.

Pyridine-derivatives. By H. Weidel and F. Blau (*Monatsh. Chem.*, **6**, 651—666).—When 30 grams of dibromopyridine are heated for 24 hours at 160° with 80 c.c. of absolute alcohol and a slight excess of potash, diethoxy- and ethoxy-hydroxypyridine are formed.

Diethoxypyridine, $C_5NH_3(OEt)_2$, forms an almost colourless oil, which is heavier than water; it is readily soluble in alcohol and ether. It boils with decomposition at 242—246° under 749·9 mm. pressure. With mineral acids, it yields crystalline salts which are very deliquescent. The *platinochloride* forms lustrous, yellow needles.

Dihydroxypyridine, $C_5NH_3(OH)_2$, is obtained by hydrolysis of the diethyl-derivative by hydriodic acid and amorphous phosphorus at 120°. It forms small, yellowish-white crystals, which become brown at 200°, almost black at 230°, and melt with total decomposition at 237—239°. It dissolves readily in hot water, alcohol, alkaline carbonates, and in dilute acids. When a neutral solution of dihydroxypyridine is treated with ferric chloride, it acquires a reddish-brown colour. The compound is probably identical with the dihydroxypyridine prepared by Geigy (*Inaug. Diss.*, Munich, 1885) from pyridinedisulphonic acid.

Ethoxyhydroxypyridine, $EtO{\cdot}C_5NH_3{\cdot}OH$, forms colourless plates, which become yellowish when exposed to light; it is sparingly soluble in water, readily in alcohol, and in a mixture of alcohol and ether. The

crystals are triclinic; $a : b : c = 0{\cdot}97408 : 1{\cdot}01795 : 1$; $\xi = 93° 1'$; $\eta = 88° 29'$; $\phi = 91° 04'$. It melts at 127—128° (uncorr.), and does not distil without decomposition. The *nitrate* and *platinochloride* are described. When fused with potash, it yields dihydroxypyridine.

Sodium ethoxide acts on dibromopyridine at 150°, with formation of diethylpyridine, together with a trace of the monethyl salt. By the action of alcoholic potash on bromopyridine (the intermediate product formed in the preparation of dibromopyridine), *ethoxypridine* was obtained; it forms a colourless liquid, which boils below 200°, and when reduced yields a hydroxypyridine, identical with that already obtained from β-pyridinemonosulphonic acid (compare Abstr., 1884, 1050 and 1370). It is therefore a meta-derivative, and the dibromo-compound obtained from it probably has both bromine-atoms in the meta-position, from the fact that it yields only one monethyl salt.

N. H. M.

Constitution of Synthetical Hydropyridine-derivatives. By A. Hantzsch (*Ber.*, **18**, 2579—2586).—The constitution of these compounds has never been definitely ascertained, although it has been assumed that both the hydrogen-atoms are in union with carbon-atoms in the pyridine-ring, thus giving the formula $N<\begin{matrix}CH\cdot CH\\C\text{——}C\end{matrix}>C$ for the nucleus of this group. Kuckert has, however, recently shown that a substituted hydropyridine-derivative is obtained by the condensation with paraldehyde and sulphuric acid of the product obtained by the action of methylamine on ethyl acetoacetate: from this it follows that the nitrogen must be exerting imidic functions, and that the constitution of the hydropyridine nucleus must be

$$HN<\begin{matrix}C : C\\C : C\end{matrix}>CH.$$

The ketone, $C_8H_{12}O$, obtained by the action of hydrochloric acid on ethyl hydrocollidinecarboxylate (Abstr., 1883, 84) when treated with hydroxylamine, yields a crystalline oximido-compound, $C_8H_{12} : NOH$.

By heating ethyl acetoacetate with benzaldehyde and methylamine, two non-nitrogenous products, $C_{19}H_{24}O_6$ and $C_{19}H_{22}O_5$, are obtained. The part played by the methylamine in the reaction is obscure, but unless it or some other primary amine is present, these substances are not formed.

Ethyl benzylidinediacetoacetate, $C_{19}H_{24}O_6 = CHPh(CHAc\cdot COOEt)_2$, crystallises in long, white needles, melts at 152—153°, and is sparingly soluble in alcohol and ether; when treated with bromine, it yields a substitution-derivative, $C_{19}H_{23}BrO_6$, melting at 159°.

Ethyl dehydrobenzylidinediacetoacetate, $C_{19}H_{22}O_5$, crystallises in lustrous prisms, melts at 87—88°, and is readily soluble in nearly all solvents. The author assigns to it the constitution

$$O<\begin{matrix}CMe : C(COOEt)\\CMe : C(COOEt)\end{matrix}>CHPh,$$

regarding it as a hydropyridine-derivative, in which the imido-group is replaced by oxygen.

A. J. G.

β-Dipyridyl. By T. Leone and V. Oliveri (*Gazzetta*, **15**, 271—277).—A dipyridyl, $C_{10}H_8N_2$, is produced by the dry distillation of pyridinesulphonic acid and separation of the distillate by concentrated potash. It crystallises in colourless prisms melting at 68°, and boiling at 286—288°; its platinochloride is an orange-yellow powder, insoluble in water, alcohol, and ether. This dipyridyl is probably identical with that obtained by Skraup and Vortmann by the dry distillation of dipyridyldicarboxylic acid (Abstr., 1883, 88), as evidenced by its direct conversion into nicotinic acid, and of the formation of the same acid from the sulphonic acid originally used. It is proposed to call it β-dipyridyl, and to assign to it the following structure:—

$$C_5H_4N\cdot C_5H_4N \quad [N : C_5H_4N = 1 : 3].$$ V. H. V.

Pyridine-choline, Pyridine-neurine, and Pyridine-muscarine. By T. Coppola (*Gazzetta*, **15**, 330—345).—The alkaloïds choline, neurine, and muscarine are analogous not only in their chemical constitution, inasmuch as they can be regarded as hydroxyethylene-, vinyl- and dihydroxyethylenetrimethyl ammonium hydroxides, but also in the physiological symptoms produced by them, namely, stimulation of the inhibitory ganglia of the heart, arrestation of the diastole, and excitation of the secretory nerves. In this paper, the chemical properties and functions of their pyridine-derivatives are described.

Pyridine-choline hydrochloride, $OH\cdot C_2H_4\cdot C_5H_5NCl$, obtained by heating a mixture of pyridine and ethylene chlorhydrin in equal molecular proportions, forms colourless, prismatic crystals, very deliquescent, and soluble in alcohol and water, insoluble in ether. Its *platino-* and *auro-chlorides* are yellow, amorphous powders; its hydroxide is very readily decomposed.

Pyridine-neurine hydriodide, $C_5H_5(C_2H_3)NI$, obtained by heating the above compound with concentrated hydriodic acid, crystallises in opaque, white prisms, very soluble in boiling alcohol and water, insoluble in ether. Its *platino-* and *auro-chlorides* are yellow amorphous powders.

Pyridine-muscarine hydrochloride, $C_2H_3(OH)_2\cdot C_5H_5NCl$, obtained from pyridine-choline by heating it with nitric acid (sp. gr. 0·148), forms orange-yellow, deliquescent laminæ; its *platinochloride* crystallises in orange-yellow needles, its *aurochloride* is an amorphous powder.

The physiological function of the above compounds is perfectly similar, in that they all arrest voluntary movements, and at first excite but afterwards paralyse the cardiac pulsations. As regards their toxic effects they differ considerably in degree. The variation of physiological function with chemical constitution, more especially as regards the effect of the substitution of hydrogen-atoms by different groups, especially hydroxyl and the choline, neurine, and muscarine radicles, is discussed at some length. V. H. V.

Isoquinoline. By S. Hoogewerff and W. A. v. Dorp (*Rec. Trav. Chim.*, **4**, 125—129).—By adding concentrated sulphuric acid to an alcoholic solution of the crude quinoline from coal-tar, the sulphates of quinoline and *isoquinoline*, C_9H_7N, are precipitated, and by repeated rectification of the free bases obtained from this precipitate two fractions are obtained, one boiling from 230° to 236°, which is chiefly

quinoline, and the other boiling from 236° to 243°, containing isoquinoline: this is purified by the repeated recrystallisation of its sulphate from alcohol. The free base melts at 18—23° and boils at 236—237·5° (uncorr.). The *sulphate*, C_9H_7N,H_2SO_4, forms hygroscopic prisms or tablets, and melts at 205—208°. The *chromate*, $(C_9H_7N)_2,H_2Cr_2O_7$, forms reddish-yellow needles, and is decomposed at about 150°. The *platinochloride*, $(C_9H_7N)_2,H_2PtCl_6 + 2H_2O$, forms slender, yellowish-red needles; it becomes anhydrous at 110°. The *picrate* is but little soluble in alcohol or water, and crystallises in yellow needles; it melts at 222—223·5°. A. P.

Constitution of Quinoline-derivatives prepared from Meta-substituted Amines. By L. Gattermann and A. Kaiser (*Ber.*, **18**, 2602—2604).—Whilst the constitution of quinoline-derivatives prepared from ortho- and para-substituted amines is certain, inasmuch as only one substance can be formed in each case; in those from meta-compounds, two quinoline-derivatives are theoretically obtainable, according as the linking of the pyridine-ring occurs at the ortho- or para-position relatively to the substituting group. It seems as though this question can be solved by the use of compounds in which one or the other of these positions is occupied by halogens, &c.

Chloromethylquinoline, C_9NH_5MeCl [Me : Cl = 1 : 4], is prepared by Skraup's method from parachlorometatoluidine; it crystallises in colourless needles, of quinoline-like odour, melts at 49°, and is soluble in water, readily soluble in ether, alcohol, and benzene. The *mercurochloride*, $C_{10}H_8NCl,HHgCl_3$, crystallises in broad needles or tables, the *platinochloride*, $(C_{10}H_8NCl)_2,H_2PtCl_6$, forms yellowish-brown tables or broad needles, the picrate crystallises in large, brownish-yellow tables, and melts at 172°. When heated with excess of hydrogen iodide dissolved in acetic acid, the chlorine is replaced and a methylquinoline obtained. The author cannot as yet speak positivel yas to the identity or non-identity of this with Skraup's "metatoluquinoline."

A. J. G.

Paraquinanisoïl. By Z. H. Skraup (*Monatsh. Chem.*, **6**, 760—784).—Paraquinanisoïl is best prepared by heating a mixture of 78 grams anisidine, 50 grams nitranisoïl, 320 grams glycerol, and 125 grams sulphuric acid for two hours; 50 grams more of sulphuric acid are added, and the heating continued for two hours longer. The product is then diluted with water, distilled with steam, and the residue treated with potassium dichromate, which causes a precipitation of quinanisoïl chromate; this is then purified. Pure quinanisoïl forms a yellowish oil, which soon acquires a green, then a reddish-violet colour; it boils with slight decomposition at 304—305° (uncorr.). Sp. gr. at 20° = 1·542 (water at 20° = 1). *Paraquinanisoïl hydrochloride*, $C_9NHOMe,HCl + 2H_2O$, forms colourless prisms, readily soluble in cold water and hot alcohol, insoluble in ether. It loses its water of crystallisation over sulphuric acid. The *chromate* forms long, gold-coloured, silky needles, which when exposed to air lose their lustre and become brownish; it is very sparingly soluble in cold water. The *neutral sulphate*, *acid sulphate*, *tartrate*, and other salts are described. The aqueous solutions of the salts all show a

blue fluorescence. Chlorine-water and ammonia act on the salts, giving the green colour characteristic of quinine compounds.

Paraquinanisoïl methiodide crystallises from water in long, gold-coloured, lustrous needles, which melt with evolution of gas at 235°. It is insoluble in ether, readily soluble in hot water and alcohol.

Thalline, $C_9H_{10}MeNO$, is prepared by reducing quinanisol with tin and hydrochloric acid; it forms thick, white prisms, sparingly soluble in water and light petroleum, very readily in alcohol, ether, and benzene. It melts at 42—43°, and boils at 283° (uncorr.; bar. = 735 mm.). When treated with ferric chloride or other oxidising agents, it acquires first a yellow, afterwards a dark emerald-green colour. Silver nitrate produces this coloration with separation of silver. *Thalline hydrochloride*, $C_{10}H_{13}NO,HCl$, crystallises in well-formed prisms, sparingly soluble in alcohol. The *sulphate* (with 2 mols. H_2O) and other salts are described. *Acetylthalline*, $C_{10}H_{12}NO{\cdot}Ac$, forms clear, broad, monoclinic prisms, which melt at 46—47°. Its solubility resembles that of thalline. Bromine acts on thalline with formation of a compound, $C_{10}H_6Br_3NO$; it is a pale yellow powder, melting at 193—194°.

Methylthalline, $C_{10}H_{12}NOMe$, is prepared by the action of methyl iodide on thalline. It forms a thick, colourless oil, which when kept becomes brown; it boils at 277—278·5° (uncorr.). When a solution in dilute hydrochloric acid is treated with ferric chloride, it acquires a cherry-red colour, which changes to reddish-yellow when kept long. The *hydrochloride* and *sulphate* crystallise in well-formed prisms, readily soluble in water.

Thaline hydriodide, $(C_{10}H_{13}NO)_2,HI$, and *quaternary dimethylthalline iodide*, $C_{10}H_{12}NOMe_2I$, are formed in the preparation of methylthalline. The former compound crystallises in flat prisms, melting at 155—156°, insoluble in ethylbenzene, light petroleum, readily soluble in hot alcohol. The latter compound forms long prisms, insoluble in light petroleum, readily soluble in alcohol and in water, from which it crystallises with 1 mol. H_2O. It melts with evolution of gas at 223—224°. Boiling aqueous potash, hydrochloric and nitric acids, do not act on it.

Ethylthalline, $C_{10}H_{12}EtNO$, is a thick oil, which boils at 287—287·5°, with slight decomposition. It is insoluble in water, very readily soluble in alcohol, ether, and in mineral acids. Some salts were prepared; they are very hygroscopic and crystallise with difficulty. *Ethylthalline ethiodide* forms white needles, readily soluble in alcohol and in water, insoluble in ether; it melts, with evolution of gas, at 131—133°; when distilled it decomposes into ethyl iodide and ethylthalline.

Benzyl chloride acts on thalline with formation of a base, probably benzylthalline; when treated with ferric chloride, it gives the same characteristic red colour as methyl- and ethyl-thalline.

The physiological properties of several of the compounds mentioned in the paper are described. The paper concludes with remarks on the constitution of quinine. N. H. M.

Para- and Ortho-phenylquinoline. By W. La Coste and C. Sorger (*Annalen*, **230**, 1—42).—*Paraphenylquinoline* is prepared by

the action of sulphuric acid, glycerol, and nitrobenzene on paramidodiphenyl. The base is precipitated from the acid solution by the addition of an alkali, collected, dried, and dissolved in warm benzene. The solution is left in contact with solid potassium hydroxide for some hours, and is then filtered. After removing the benzene by distillation, the residue is distilled under reduced pressure. Paraphenylquinoline, C_9NH_6Ph [Ph = 3], melts at 110—111° and boils at 260° under 77 mm. pressure; its sp. gr. is 1·1945 at 20°. It is sparingly soluble in water, but dissolves freely in alcohol, chloroform, benzene, and carbon bisulphide. Phenylquinoline is deposited from ether in rhombic pyramids, from alcohol in combinations of the pyramid and basic plate, and from benzene in twin pyramids; all the salts are soluble in water, forming fluorescent solutions. The *tartrate*, $C_9NH_6Ph,H_2C_4H_4O_4 + 3H_2O$, crystallises in needles, melting at 153°. The *dichromate*, $(C_9NH_6Ph)_2,H_2Cr_2O_7$, forms reddish-yellow needles, which melt at 136°. The *methiodide*, $C_9NH_6Ph,MeI + 2H_2O$, crystallises in long needles melting at 194°. The *ethiodide* crystallises with 2 mols. H_2O in pale yellow needles, and also with 1 mol. H_2O in thick, yellow prisms.

When phenylquinoline is treated with tin and hydrochloric acid, it unites with four atoms of hydrogen to form a tetrahydro-compound. The *hydrochloride*, $C_9NH_{10}Ph,HCl + 1\frac{1}{2}H_2O$, crystallises in needles. It is sparingly soluble in cold water, and is partially decomposed by hot water. It also dissolves in alcohol and in chloroform.

The free base is soluble in alcohol, ether, and hot water. The *picrate*, $C_9NH_{10}Ph,C_6H_2(NO_2)_3{\cdot}OH$, is deposited from a hot aqueous solution in needles which dissolve freely in alcohol, chloroform, and benzene. It melts at 165°.

The *nitroso*-compound, $C_9NH_9Ph{\cdot}NO$, forms yellow crystals, freely soluble in benzene and chloroform. The *acetyl*-derivative, C_9NH_9PhAc, crystallises in white, silky needles. It melts at 100°, and is freely soluble in alcohol, benzene, chloroform, and carbon bisulphide.

The *benzoyl*-derivative forms white plates melting at 137°. It is freely soluble in alcohol.

Methyltetrahydroparaphenylquinoline hydrochloride,

$$C_9NH_9MePh,HCl,$$

prepared by the action of tin and hydrochloric acid on phenylquinoline methochloride is a crystalline substance, soluble in alcohol and chloroform. The *platinochloride* easily decomposes.

The *hydriodide*, C_9NH_9MePh,HI, resembles the hydrochloride, but is more easily decomposed by water. The *picrate* melts at 147°. It dissolves in alcohol, chloroform, and benzene. The *methiodide* melts at 194°. It crystallises in plates or prisms, soluble in alcohol and in chloroform.

The substitution products of paraphenylquinoline do not crystallise easily, and can only be prepared with difficulty in the pure state. The *mononitro-derivative*, $C_{15}NH_{10}{\cdot}NO_2$, is formed by the action of fuming nitric acid on an acetic acid solution of paraphenylquinoline. It melts at 173°, and is soluble in alcohol, ether, benzene, and in hot water. The compound also dissolves in dilute acids, and forms two

crystalline platinochlorides, of which one is insoluble in hot water. The *dinitro*-compound is obtained by adding phenylquinoline to fuming nitric acid. It melts at 208°, and dissolves in alcohol and benzene.

Phenylquinoline dissolves in cold fuming sulphuric acid, yielding two isomeric monosulphonic acids. The *α*-sulphonic acid, $C_{15}H_{11}NSO_3 + 2H_2O$, can be separated from its isomeride by the greater solubility of the latter, and also of its ammonium salt in water. The *α*-acid crystallises in long needles, soluble in hot water. It does not melt at 300°. When oxidised with potassium permanganate, it yields parasulphobenzoic acid. The ammonium salt of *α*-phenylquinolinesulphonic acid crystallises in plates, which dissolve freely in hot water. The sodium and calcium salts dissolve freely in water, the potassium and barium salts are sparingly soluble. *β-Phenylquinolinesulphonic acid*, $C_{15}H_{11}NSO_3 + H_2O$, dissolves freely in water, but is insoluble in chloroform and ether. The *ammonium* salt crystallises in anhydrous scales.

Orthophenylquinoline, C_9NH_6Ph [Ph = 1], is prepared by a process analogous to that employed in the preparation of the para-compound. It is a thick, fluorescent oil, which darkens on exposure to the air. It dissolves freely in alcohol, ether, benzene, carbon bisulphide, and chloroform, and boils between 270° and 276° under a pressure of 80 mm.

The salts of the base are soluble in water, forming fluorescent solutions. The *platinochloride* crystallises in needles; the *dichromate* in plates, melting at 126°, and dissolving in water and warm alcohol. The methiodide forms reddish-yellow plates melting at 163°. It is freely soluble in water, alcohol, and chloroform. *Orthophenylquinolinemethyl platinochloride*, $(C_9NH_6PhMe)_2PtCl_6$, is a crystalline salt, soluble in hot water. It melts at 192°. W. C. W.

Colouring Matters derived from the Quinoline Bases. By O. de Coninck (*Rec. Trav. Chim.*, **4**, 58—60).—The reaction of an alcoholic solution of potassium hydroxide on the iodides of the ethyl and methyl derivatives of the quinoline bases, by which a red colouring matter is produced (*Rec. Trav. Chim.*, **3**, 337), appears to be general for all the alkyl-derivatives of quinoline, as the author has prepared a red crystalline colouring matter from the iodide of the propyl-derivative; he also confirms the constitution assigned to the cyanine-derivatives obtained by the action of potassium hydroxide on the iodide of ethyl-lepidine and ethylquinoline (Abstr., 1885, 673). A. P.

Quinoxalines. III. By O. Hinsberg (*Ber.*, **18**, 2870—2875).—*Dihydro-oxytoluquinoxaline*,

$$C_7H_6<\begin{matrix}NH\cdot CH_2\\NH\cdot CO\end{matrix}> \text{ or } C_7H_6<\begin{matrix}-NH\cdot CH_2-\\N:C(OH)\end{matrix}>,$$

is obtained by heating ethyl chloracetate (2 mols.) with toluylenediamine (3 mols.) for several days on a water-bath, and is purified by means of its sparingly soluble sodium-derivative. It crystallises in moderately large, yellowish needles, is readily soluble in hot water

and alcohol, moderately in ether, and also in alkalis and acids. The potassium-derivative is readily soluble in water and in potash solution; the sodium-derivative, $C_9H_9N_2ONa + H_2O$, forms lustrous scales, and is almost completely precipitated from its aqueous solutions by the addition of soda. Dihydro-oxytoluquinoxaline in alkaline solution is oxidised by atmospheric oxygen to hydroxytoluquinoxaline; neutral solutions are not so readily acted on, but are also oxidised by weak oxidising agents.

When toluylenediamine and ethyl chloracetate are heated together in equal molecular proportions, the compound $C_{13}H_{16}N_2O_3$ is produced, and may be purified by crystallisation from alcohol. It forms colourless, lustrous scales, melts at 147°, is sparingly soluble in water, nearly insoluble in ether, and moderately soluble in alcohol. Concentrated mineral acids and acetic acid dissolve it readily, whilst alkalis dissolve it only on warming. Silver nitrate and nitrous acid oxidise it apparently to a product melting at 247—248°. On saponifying the substance $C_{13}H_{16}N_2O_3$ with alkali, a sparingly soluble acid is obtained, crystallising in white needles. The formation and constitution of the above compound may probably be expressed thus:—

$$2C_7H_6(NH_2)_2 + 2CH_2Cl\cdot COOEt = <\begin{matrix}NH\cdot C_7H_6\\ CH_2—CO\end{matrix}>N\cdot CH_2\cdot COOEt + EtOH + C_7H_6(NH_3Cl)_2.$$

A. K. M.

Papaverine. By C. Goldschmiedt (*Monatsh. Chem.*, **6**, 667—701; compare Abstr., 1885, 1080).—Analyses of papaverine and of a large number of its salts, confirm the correctness of the formula $C_{20}H_{21}NO_4$ assigned to papaverine by Merck and others. Papaverine crystallises in rhombic prisms, $a : b : c = 0{\cdot}3193 : 1 : 0{\cdot}4266$. Crystallographic measurements of various derivatives and salts are also given.

N. H. M.

Hydrobromapoquinine. By P. Julius (*Monatsh. Chem.*, **6**, 750—753).—*Hydrobromapoquinine*, $C_{19}H_{23}BrN_2O_2$, is prepared by heating quinine hydrate at 100° with three times its weight of water saturated with hydrobromic acid at 0°. It forms a white amorphous powder, which melts at 209—210°, is insoluble in water, readily soluble in alcohol. The *hydrobromide*, $C_{19}H_{23}BrN_2O_2,2HBr + H_2O$, crystallises in groups of white needles, readily soluble in water and in alcohol. The *platinochloride* is described.

N. H. M.

Cupreine and Homoquinine. By O. Hesse (*Annalen*, **230**, 55—73).—The author confirms the accuracy of his former statement (Abstr., 1885, 276) that homoquinine is a compound of quinine and the new alkaloïd discovered by Paul and Cownley, called cupreine. Many of the properties of cupreine have been already described. The base crystallises with 2 mols. H_2O, which are expelled at 120°. The anhydrous substance melts at 198°. The alcoholic solution gives a dark reddish-brown coloration with ferric chloride, and an intense green coloration with chlorine and ammonia. The neutral salts of cupreine dissolve in water, forming yellow solutions, which are rendered colourless by the addition of acids. The solutions are not

fluorescent. The neutral sulphate, $(C_{19}H_{22}N_2O_2)_2,H_2SO_4 + 6H_2O$, crystallises in needles; the hydrogen sulphate, $C_{19}H_{22}N_2O_2,H_2SO_4 + H_2O$, forms flat prisms, sparingly soluble in cold water. There are two hydrochlorides, $C_{19}H_{22}N_2O_2,HCl + H_2O$, crystallising in colourless needles, and $C_{19}H_{22}N_2O_2,2HCl$, forming pale yellow prisms. The normal platinochloride, $(C_{19}H_{22}N_2O_2)_2,H_2PtCl_6 + 4H_2O$, is amorphous; the acid salt forms orange-coloured plates. The normal tartrate and thiocyanate are sparingly soluble in water. Cupreine does not combine with ammonia, but it forms compounds with potassium, sodium, lead, and silver.

Anhydrous cupreine dissolves in acetic anhydride, forming a *diacetyl* compound, $C_{19}H_{20}Ac_2N_2O_2$, crystallising in six-sided plates. It melts at 88°, and is soluble in alcohol, ether, and chloroform. The hydrochloride also crystallises in six-sided plates, soluble in alcohol and water.

Cupreine is converted into apoquinine by the action of hydrochloric acid at 140°. *Cupreine methiodide* forms colourless crystals, sparingly soluble in cold alcohol and water. The corresponding chloride, $C_{15}H_{22}N_2O_2,MeCl$, and platinochloride, $C_{19}H_{22}N_2O_2,MeHPtCl_6 + 2H_2O$, are also crystalline. The sulphate crystallises in needles, which are freely dissolved in water. By decomposing this salt with baryta-water, the hydroxide is obtained. The aqueous solution of the hydroxide gives a red coloration with excess of bleaching powder in presence of ammonia, and a green coloration when ammonia is added to a mixture of the acidified solution and a small quantity of bleaching powder.

The alcoholic solution of the hydroxide is fluorescent.

Homoquinine is easily prepared by adding ammonia to a solution of equal molecular weight of quinine and cupreine in dilute sulphuric acid, and dissolving the precipitate in ether. Homoquinine is not a simple alkaloïd, but a compound of the composition

$$C_{20}H_{24}N_2O_2,C_{19}H_{22}N_2O_2 + 4H_2O.$$ W. C. W.

Cocaïne and its Salts. By B. H. Paul (*Pharm. J. Trans.* [3], **16**, 325—326).—The author's experiments indicate that the solubility of cocaïne in water is much less than 1 in 700; moreover, that on evaporating the aqueous solution the cocaïne is decomposed, leaving a gummy mass, which crystallises and has many properties similar to those attributed to ecgonine (compare Merck, Abstr., 1885, 997). It yields benzoïc acid by the action of caustic soda, lime, or sodium carbonate, but not apparently by the action of hydrochloric acid. It combines with benzoïc acid, but can be separated from the acid by repeated crystallisation from water. Cocaïne hydrochloride is only slightly soluble in water, from which solution it can be crystallised with water of crystallisation, but after prolonged heating on a water-bath it remains in a resinous state, for a considerable time at least. The acetate is very soluble, and is difficult to crystallise, owing to the volatilisation of the acetic acid during evaporation. The solution of the benzoate dries to a thick, gummy residue. Ammonia precipitates the alkaloïd without apparent decomposition, and when added in excess does not redissolve it. D. A. L.

Alkaloïds from Erythroxylon. By C. J. Bender (*Chem. Centr.*, 1885, 490—493).—The author has subjected the leaves of the coca-plant (*Erythroxylon coca*) to a careful investigation. Besides cocaïne, he obtained an amorphous alkaloïd to which he gives the name *cocaïcine*, and a volatile base which he names *erythroxyline*. There also seem to be one or two other alkaloïds present, but the author was unable to obtain them in a pure state, or to determine whether they were present in the fresh leaves or formed during the process of extraction. L. T. T.

Bases in Jaborandi Leaves. By E. Harnack (*Chem. Centr.*, 1885, 628—629).—Besides pilocarpine and jaborine, Merck (Harnack and Meyer, Abstr., 1880, 898) obtained from the leaves of the jaborandi a third syrupy alkaloïd, which yielded a nitrate crystallising in well-defined prisms. The author has investigated this alkaloïd, to which he gives the name *pilocarpidine*. It very closely resembles pilocarpine, both in physiological and chemical properties, but it does not give a precipitate with auric chloride. Its formula is $C_{10}H_{14}N_2O_2$. It is easily converted into an amorphous base, *jaboridine*, $C_{10}H_{12}N_2O_3$, which resembles jaborine and atropine in properties. Jaboridine appears to be identical with jaborandine, $C_{10}H_{12}N_2O_3$, obtained by Parodi (*Rivista farm.*, 1875, 3) from false jaborandi (*Piper jaborandi*), and by Chastaing, by the oxidation of pilocarpine with fuming nitric acid. The author believes that the jaborine hitherto obtained has always contained jaboridine as an impurity. From the formula and properties of pilocarpine, $C_{11}H_{16}N_2O_2$, this substance would appear to be a methyl-derivative of pilocarpidine; and the author points out that the latter has the composition of a di-hydroxy-derivative of nicotine or of an isomeride thereof. Jaboridine is an oxidation product of pilocarpidine, formed by the replacement of two atoms of hydrogen in the latter by an atom of oxygen.

L. T. T.

Alkaloïds of Fenugreek Seeds. By E. Jahns (*Ber.*, **18**, 2518—2523).—The seeds of *Trigonella fœnum græcum* contain trigonelline and a liquid base identified as choline. *Trigonelline*, $C_7H_7NO_2 + H_2O$, crystallises in colourless, flat prisms, of feeble saline taste; it is readily soluble in water, sparingly soluble in cold alcohol, insoluble in ether, chloroform, and benzene; it is carbonised when heated. The reactions with the various reagents for alkaloïds are described. The hydrochloride, $C_7H_7NO_2,HCl$, crystallises in anhydrous tables; the platinochloride, $(C_7H_7NO_2)_2,H_2PtCl_6$, crystallises in prisms. Two aurochlorides were obtained, $C_7H_7NO_2,HAuCl_4$, crystallising in four-sided plates or flat prisms, and melting at 198°, and $4C_7H_7NO_2,3HAuCl_4$, crystallising in slender needles and melting at 186°. A. J. G.

Products of the Action of Hydrochloric Acid on the Albuminoids. By J. Horbaczewski (*Monatsh. Chem.*, **6**, 639—650).—When 500 grams of elastin (previously freed from fat by extracting the finely powdered substance for two weeks with ether), are boiled for 72 hours with 1 litre of hydrochloric acid diluted with an equal

volume of water and 25 grams of zinc chloride, a small quantity of ammonia is given off, and the solution after precipitation of the zinc by hydrogen sulphide is found to contain leucine, glycocine, and tyrosine. Other compounds are also present, but could not be isolated. The formation of these substances, and the absence of glutaminic and aspartic acids and of hydrogen sulphide from the product of the reaction, show that elastin does not belong to the same class of compounds as do albumin and keratin. It also differs from the horn substances and all other albuminoïds which have as yet been examined. N. H. M.

Physiological Chemistry.

Digestion of Cellulose. By W. Henneberg and F. Stohmann (*Zeit. Biol.*, **21**, 613—624).—The author's discussion of this subject has special reference to the recent investigations of Tappeiner (*ibid.*, **20**, 52), which have shown that the main products of fermentation of cellulose, excluding the gases, are acetic and butyric acids. Having pointed out certain errors in the statement of the results of his experiments, they substitute the following:—

Carbonic anhydride	33·63
Marsh-gas	4·70
Hydrogen	0·35
Acetic acid	33·51
Butyric acid	33·63
Total products	105·82

which may be summed up in the equation—

$$21C_6H_{10}O_5 + 11H_2O = 26CO_2 + 10CH_4 + 6H_2 + 19C_2H_4O_2 + 13C_4H_8O_2.$$

In regard to the utilisation of molecular energy, the above resolution may be expressed as under:—

100 grams cellulose (100 × 4146)	414,600 cal.
33·5 Carbonic anhydride	0
4·7 Marsh-gas (4·7 × 13344)	62717
33·6 Acetic acid (33·6 × 3505)	117768
33·6 Butyric acid (33·6 × 5647)	189739
Heat of resolution	44376
	414600

Supposing with Tappeiner that the marsh-gas is excreted directly,

which, however, is by no means certain, and consequently that the corresponding amount of energy, 15 per cent. of the whole, is lost to the organism, cellulose would still seem to be a food-stuff of high value, apart from any subsidiary mechanical functions which it may perform in digestion.

The authors have assumed the correctness of Tappeiner's experimental results as the basis of this discussion; at the same time they do not admit that he has established his position. There is still a probability that in the hydrolysis of cellulose intermediate products belonging to the carbohydrate group are formed, which, at least in part, are directly assimilated. C. F. C.

The Presence of Glycogen in the Protozoa. By O. Bütschli (*Zeit. Biol.*, **21**, 603—612).—The author's experiments were undertaken as a confirmation of previous investigations which have been recently criticised by Frenzel (*Arch. f. Mikr. Anat.*, **24**, 545). The subject in question is the composition of the granules of the entoplasm of the gragorinæ. From a number of qualitative results (of a somewhat indefinite character), the author concludes that the substance composing these granules is glycogen, or a compound of similar nature ("paraglycogen"). The author has identified such a substance also in the infusoria Nyctotherns, Ovalis, and Strombidium, confirming, therefore, the observations of Certes (*Compt. rend.*, **90**, 70).

C. F. C.

Albuminoïd Substance in Urine. By F. Müller (*Chem. Centr.*, 1885, 597—598).—This substance is precipitated from urine by acetic acid, and is regarded as a modification of albumin by the author, as it is precipitated both by magnesium sulphate, and on boiling; moreover it resembles other albuminoïd bodies in its behaviour with nitric acid. P. P. B.

Amount of Volatile Acids in the Excrements of Ruminants. By H. Wilsing (*Zeit. Biol.*, **21**, 625—630).—The author's experiments were undertaken as a development of Tappeiner's observations on the formation of acetic and butyric acids as the main products of the digestive hydrolysis of cellulose. The subject of the experiments was a goat receiving 1·5 kilo. meadow hay per diem; the results obtained are summarised in the following table:—

Experiment.	Urine.			Fæces.		Aggregate.
		Volatile acids.				
	Total in 24 hours.	Total.	Excl. HCl + Ph·COOH.	Total in 24 hours.	Vol. acids.	Vol. fatty acids.
I	992	2·937	2·201	?	1·802	4·003
II	830	2·854	2·175	?	1·802	3·997
III	815	1·444	0·935	565	1·800	2·735
IV	1241	3·711	2·934	668	1·803	4·737
V	812	1·859	1·270	?	1·802	3·072

The hay contained 25·9 "crude fibre," of which 60 per cent. was found to disappear in the process of digestion, whence, the author states, 233 grams *cellulose* are digested in the 24 hours; and as this quantity would yield, according to Tappeiner's observations, 157 grams volatile fatty acids, it is seen that of the latter 97·4 per cent. are assimilated, and 2·6 per cent. only excreted. C. F. C.

Abstractor's Note.—It is to be observed that agricultural chemists continue to apply the term cellulose collectively to plant fibres, disregarding the variations in composition of the fibre substance.

Pathological Urine. By A. Villiers (*J. Pharm.* [5], **11**, 246—249).—Contrary to Bouchard and Pouchet, the author finds that normal urine never contains alkaloïds. Operating always on two litres, he first evaporated by heat, then in a vacuum, took up the residue with absolute alcohol, evaporated the filtered alcoholic solution in a vacuum, and took up this second residue with a drop of water. In this solution, the alkaloïds were detected by alternate precipitation with an alkaline carbonate in presence of ether, and re-solution in water acidified with hydrochloric acid. When care was taken to obtain normal urine, the results were always negative, but alkaloïds were found in the urine when the subject was suffering from a slight attack of bronchitis, indisposition with fever, measles, pneumonia, abscess in the head; in one case of tetanus, alkaloïds were not found. J. T.

Physiological Action of Rubidium Salts. By C. Richet (*Compt. rend.*, **101**, 667—669).—The toxic effect of rubidium chloride depends on the mode of introduction into the system. If the solution is injected under the skin, the minimum fatal dose is about 1 gram per kilo. of body weight, but if injected directly into the veins, about 0·5—0·6 gram per kilo. of body weight is sufficient to cause death. In both cases the poison acts directly on the heart and stops its movements. Rubidium is less poisonous than potassium. C. H. B.

Physiological Action of Salts of Lithium, Potassium, and Rubidium. By C. Richet (*Compt. rend.*, **101**, 707—710).—Aqueous solutions of the chlorides of the three metals were injected under the skin of various animals, and the minimum dose sufficient to cause death was determined. The effects of lithium chloride appear very slowly, but the action of rubidium and potassium chlorides is evident in a few hours. Leaving out crayfish, which are very easily poisoned by the chlorides, and snails, which offer considerable resistance to their action, it was found that the minimum fatal dose per kilo. of body weight was practically the same for tench, tortoises, frogs, pigeons, guinea-pigs, and rabbits, being 0·1 gram for lithium,* 0·5 for potassium, and 1·0 for rubidium. These numbers are almost in exactly the same ratio as the atomic weights of the three metals, namely, 7, 39, and 85. In other words, lithium, potassium, and rubidium, if taken in molecular proportion instead of in equal weights,

* These numbers represent, not the amount of chloride, but the amount of metal in the form of chloride.

are equally poisonous. It would seem, therefore, that the toxic action is really a chemical action, and it is probable that these three chlorides act by displacing, molecule for molecule, the sodium chloride present in the tissues. C. H. B.

Physiological Action of Liebig's Extract of Meat. By K. B. Lehmann (*Chem. Centr.*, 1885, 665).—Neither this extract nor potassium salts, even when taken in large doses, have a specific action on the rate, strength, or regularity of the pulse. The action which has been observed is only the general reflex action of all salts on the stomach and intestines. The continued consumption of large quantities of the extract, even up to 1 per cent. of the whole weight of the body, had not an ill, but apparently a very favourable effect. L. T. T.

Adipocere. By E. Zillner (*Chem. Centr.*, 1885, 441—442).—From the results of several minute microscopical and chemical investigations the author concludes that adipocere is formed from the various fats present in the body at the moment of death, and that the albuminoïds do not play any part in this transformation. After a few months' putrefaction, the animal tissues are no longer impervious to the transmission of the fat, which then wanders and collects in masses, there to undergo further decomposition, and eventually lose its glycerol and oleic acid, leaving a crystallised fatty acid behind. To this end thorough moistening of the corpse is necessary to carry away mechanically the liquid products. As the crystallised acid occupies a much greater space than the amorphous form, the apparent transformation of parts of the body into fat is explained.

J. K. C.

Post-mortem Imbibition of Arsenic. By F. S. Sutton (*Amer. Chem. J.*, **7**, 75—87).—But little is known of the distributiou of arsenic and other poisons when introduced into the body after death, it being generally assumed that the transfusion of arsenic is prevented by the sulphuretted hydrogen evolved by the decomposition. That it can travel to the liver and some other viscera when injected into the stomach or rectum has been pointed out, but whether it can reach the brain is a contended point; if this is impossible, and Scolosuboff's statement that arsenic is deposited during life in the brain and spinal cord is true, then a means is afforded of distinguishing between poisoning by arsenic and post-mortem injections containing it.

The author made injections of 3 grains arsenious oxide into the stomach and rectum of dogs killed by chloroform 24 hours previously, and found that after burial for periods of from 3 to 102 days, arsenic could be detected in the liver, the kidneys, and the brain, and that the longer the time of burial, the greater was the quantity of arsenic, especially in the case of the brain. H. B.

Chemistry of Vegetable Physiology and Agriculture.

Invert Sugar and Selective Fermentation. By E. Maumené (*Compt. rend.*, **101**, 695).—A contribution to the controversy between Berthelot, Leplay, and Maumené on this subject (Abstr., 1885, 1003, 1085, 1152).

Comparative Researches on the Formation of Amides during the Germination of Various Seeds in the Dark. By B. Schulze and E. Flechsig (*Landw. Versuchs-Stat.*, 1885, 137—149).—Although we are in possession of much information concerning the change of albumin into asparagine, yet we are still ignorant whether the whole of the albuminoïds are converted into asparagine and its congeners or not. One special object of this investigation was to discover if, when legumes and cereals germinate in the dark under the same conditions, relatively corresponding amounts of amides were produced from the albumin in each. All the details of the methods employed and of the analytical results are given. The analyses show that in all cases the conversion is very gradual and different, the legumes as a rule producing, not only absolutely but also relatively, larger quantities of amides; this is most remarkable in the case of lupines. It may also be taken for granted that seeds when germinating do not of necessity produce an amount of amides at all proportional to their nitrogen reserve matter, but that the individual character of the plant itself has very considerable influence. E. W. P.

Action of Saline Solutions on Germination. By M. Jarius (*Landw. Versuchs-Stat.*, 1885, 149—178).—These experiments were instituted with the object of completely answering the question as to whether the solutions of manures in the soil have, or have not, a detrimental action on the germination of the seed sown. The first portion of the article is occupied in discussing and reviewing other work on the subject, after which the author's own experiments and results are given in very full detail. The strengths of the saline solutions employed were 0·41, 1·0, and 2·0 per cent., and the seeds were in some cases allowed to soak for 24—48 hours, and in other cases 1—5 days. The solutions employed were of sodium and potassium chlorides, potassium and ammonium sulphates, calcium hydrogen phosphate, potassium and sodium nitrates, and a solution containing all the nourishing constituents of plants. Peas steeped in a 2 per cent. solution for 24—48 hours increase in weight and volume regularly, but this increase is less than that which takes place when distilled water is employed. After 48 hours, the volume experiences a lesser increase than the weight, and this increase is reduced as the solutions become more concentrated, and the longer the period of steeping is continued, so that the ratio between volume and weight in 2 per cent. solutions and after 48 hours is the widest, that is, the

sp. gr. is then the highest. The sp. gr., as also the increase in weight and volume, is after 24 hours now raised, now lowered, when solutions of 0·2, 0·4, and 1 per cent. are used. Only in the cases of sodium chloride and nitrate in all concentrations, and from the beginning to the end of the steeping, is a constant increase in sp. gr. found; whilst in the other solutions under all conditions, the increase in weight and volume is less than that when the liquid is water. The greatest amount of variation is found in the 0·4 and 1·0 per cent. solutions of salts of potassium after 24 hours. Finally the increase in weight and volume of peas attains its maximum in the shortest possible time the more concentrated the solutions are; the time being dependent on the salt dissolved.

The influence of the solutions on germination was tested under various conditions, such as 1—5 days with full and partial supply of air. The results are as follows: germination is decidedly aided by 0·2—0·4 per cent. solutions, but 1—2 per cent. solutions do harm, the shoots being feeble and abnormal, &c.; this harmful action is the more marked when there is not a plentiful supply of air, and also the good done by the weaker solutions is less when air is not freely accessible to the seed. Leguminosæ and Cruciferæ are much assisted by the "nutritive solution," 0·4 per cent. solutions of potassium nitrate, and sodium chloride, whilst even 0·2 and 0·4 per cent. solutions of ammonium sulphate and calcium hydrogen phosphate are distinctly harmful to the above classes of plants. Grass seeds are not liable to much harm. Even 2 per cent. solutions are productive of good, the most damage being done by sodium chloride and nitrate in 2 per cent. solutions; summer rye is less subject to influence, whilst maize is more easily affected for good by 0·4 and 1·0 per cent. solutions than all the other grasses. The results of the investigation show that no harm can possibly come of the use of manures, as their solution in the soil can never be stronger than 0·4 per cent. Still the seed should not be sown immediately on the manure, as in such a case it is possible that a solution stronger than 0·4 per cent. may be formed. There is an interesting table given showing the ratio between the growths of the radicle and plumule of several seeds when subject during growth to various strengths of a solution. E. W P.

Composition of the Pollen of the Common Pine. By A. Von Planta (*Landw. Versuchs-Stat.*, 1885, 215—230).—The author fully describes every process which he has employed for the estimation of the constituents of pollen: the results are as follows:—

Water	7·66 per cent.
N	2·65 ,,
(N × 6·25	16·56) ,,
Non-nitrogenous matter	72·48 ,,
Ash	3·30 ,,
Hypoxanthine and guanine	0·04 ,,
Saccharose	11·24 ,,
Starch	7·06 ,,
Cuticula	21·97 ,,

Wax-like compounds	3·56 per cent.
Fatty acids	10·63 „
Resinous bitter compounds..	7·93 „

Under the name cuticula is to be understood that chemically changed cellular matter, which overlays structures, and is in direct contact with the air. It was estimated by digesting the pollen for three days with a 5 per cent. alcoholic potash solution, whereby fat, &c., was removed from the pollen grains; the residue was boiled with semi-normal hydrochloric acid for two hours; this removed the last traces of starch, and then ether removed any further soluble matters there might be, so that pure cuticula remained. E. W. P.

The Sugar of Symphoricarpus Racemosa. By P. Herrmann and B. Tollens (*Annalen*, **230**, 50—55).—The authors have examined the sugar contained in the fruit of *Symphoricarpus racemosa*, and find that it consists of a mixture of dextrose and lævulose. W. C. W.

Conditions of the Development, and of the Activity, of Chlorophyll. By J. H. Gilbert (*Brit. Assoc.*,* 1885).—The foliage of different plants presents a great variety of shades of green, and it may be stated that, at any rate so far as our common agricultural plants are concerned, somewhat characteristic shades of colour are shown according to the natural order to which they belong, the Leguminosæ differing from the Graminæ, the Cruciferæ, the Chenopodiaceæ, and so on. But the same description of plant will exhibit very characteristic differences, not only at different stages of growth, but at the same stage in different conditions of luxuriance, as affected by the external conditions of soil, season, manuring, &c., but especially under the influence of different conditions as to manuring.

The Rothamsted field experiments show that in a series of comparable experiments with the same crop, depth of green colour by no means necessarily implies a finally greater amount of carbon assimilation; whilst it has long ago been experimentally proved that the deeper colour was associated with a relatively high percentage of nitrogen in the dry or solid substance of the herbage; and this obviously means a lower relation of carbon to nitrogen.

Comparative determinations of the amounts of chlorophyll were made by Russell in parallel specimens to those in which the author determined the percentages of dry matter and of nitrogen.

The following table gives the results of some of these experiments; namely, the percentages of nitrogen, and the relative amounts of chlorophyll, in the separated gramineous, and the separated leguminous plants, in the mixed herbage of grass land, in specimens of wheat grown by a purely nitrogenous manure, and by the same nitrogenous manure with a full mineral manure in addition; and in specimens of barley grown by a purely nitrogenous manure, and by a mixture of the same nitrogenous manure and mineral manure in addition. It is to be borne in mind that the specimens were collected

* Read in Section B, at the meeting of the British Association at Aberdeen, September, 1885.

whilst the plants were still quite green, and actively growing. It should be further explained that the amounts of chlorophyll recorded are, as stated in the table, relative and not actual; that is to say, the figures show the relative amounts for the individual members of each pair of experiments, and not the comparative amounts as between one set of experiments and another.

	Nitrogen per cent. in dry substance.	Relative amounts of chlorophyll.	Carbon assimilated per acre per annum.	
			Actual.	Difference.
Hay.			lbs.	lbs.
Gramineæ	1·190	0·77	—	—
Leguminosæ	2·478	2·40	—	—
Wheat.				
Ammonium salts only	*1·227	2·00	1398	
Ammonium salts and mineral manure	*0·566	1·00	2222	− 824
Barley.				
Ammonium salts only	*1·474	3·20	1403	
Ammonium salts and mineral manure	*0·792	1·46	2088	− 685

* Not fully dried.

Thus the separated leguminous herbage of hay contained a much higher percentage of nitrogen in its dry substance than the separated gramineous herbage; and also a much higher proportion of chlorophyll. Indeed, under comparable conditions, the Leguminosæ eventually maintain a much higher relation of nitrogen to carbon than the Gramineæ; in other words, in their case, carbon is not assimilated in so large a proportion to the nitrogen taken up.

The wheat plants manured with ammonium salts alone show a much higher percentage of nitrogen than those manured with the same amount of ammonium salts, but with mineral manure in addition. The high proportion of chlorophyll again goes with the high nitrogen percentage; but the last column of the table shows that, with the ammonium salts without mineral manure, with the high percentage of nitrogen, and the high proportion of chlorophyll, in the dry substance of the green produce, there is eventually very much less assimilation of carbon. The result is exactly similar in the case of barley.

It is evident that the chlorophyll formation has a close connection with the amount of nitrogen assimilated, but that the carbon assimilation is not in proportion to the chlorophyll formed, if there be not a sufficiency of the necessary mineral constituents available. No doubt there had been as much, or more, of both nitrogen assimilated,

and chlorophyll formed, over a given area, where the mineral as well as the nitrogenous manure had been applied, the lower proportion of both in the dry matter being due to the greater assimilation of carbon and consequent greater formation of non-nitrogenous substances.

It is of interest to observe that these results of experiments in the field are perfectly consistent with those obtained by vegetable physiologists in the laboratory; they having found that the presence of certain mineral, or ash constituents, and especially that of potassium, is essential for the assimilation of carbon, no starch being formed in the grains of chlorophyll without the aid of that substance. Sachs says, "Potassium is as essential for the assimilating activity of chlorophyll as iron for its production."

Adonis Vernalis and Adonidin. By J. Mordagne (*Pharm. J. Trans.* [3], **16**, 145—146).—*Adonis vernalis* amongst other substances contains aconitic acid and a glucoside, adonidin. To obtain the latter, the leaves and stalks are dried, extracted with 58° alcohol, treated with basic lead acetate, the excess of lead removed with sodium carbonate, the liquid made alkaline with ammonia, and the glucoside precipitated by means of tannin. The tannate is digested with zinc hydroxide and alcohol at a gentle heat for several hours, the alcohol is then distilled off, and the glucoside extracted with absolute alcohol, carefully evaporated and dried over sulphuric acid. The yield is 2 grams per 10 kilos. The substance forms a rather hygroscopic canary-yellow powder, but after prolonged desiccation forms radiating crystals. Ammonia prevents crystallisation. It is soluble in water, alcohol, and amyl alcohol; insoluble in anhydrous ether, chloroform, turpentine oil, and benzene; and has a persistent bitter taste. Heated at 80—85° it loses 3·14 per cent. water, but does not alter physically; between 85—90° it becomes brown; and at 100° nearly black. It contains no nitrogen, is neutral to litmus, and only reduces Fehling's solution when heated with it in presence of hydrochloric acid. Ammonia turns it brown, tannin precipitates it, and basic lead acetate produces a cloudiness in its solutions, whilst baryta and alkaloïd reagents do not react with it. When decomposed, it yields a resinous substance soluble in ether, and develops a persistent odour of cut hay. Owing to its imperfect and troublesome crystallisation a good sample can scarcely be obtained for analysis, but the mean of several experiments gives per cent. C, 42·623; H, 7·547; O = 49·830.

D. A. L.

Arum Italicum. By G. Spica and G. Biscaro (*Gazzetta*, **15**, 238—242).—As the symptoms occurring in three cases of poisoning by eating the spadices of the *Arum italicum* were peculiar, the authors have made a chemical and a physiological study of this species. From the spadices, a glucoside has been extracted, identical with saponin; the symptoms produced by the hypodermic injection of both substances into frogs were compared, and found to be practically the same. In both cases, general paralysis of the nervous and muscular systems supervened, ending, in most cases, in death: the symptoms are not those of tetanus as at first supposed.

V. H. V.

Researches on Gourds. By R. Ulbricht (*Landw. Versuchs-Stat.*, 1885, 230—240).—The author details the physical composition of many gourds, showing the proportion of rind to flesh and seed, and the chemical constituents of all parts of various gourds, as well as the composition of the ash. E. W. P.

Illicium Religiosum. By J. F. Eijkman (*Rec. Trav. Chim.*, **4**, 32—54).—The liquid obtained by distilling the leaves and fruits of *Illicium religiosum* with water consists of eugenol, a terpene to which the author gives the name of *schikimene*, and safrole, besides a small quantity of some indefinite compounds of high boiling point, which are probably formed by the polymerisation of the previous compounds. Schikimene boils at about 170°, and is a fragrant, limpid, mobile, colourless liquid; its sp. gr. = 0·865; with concentrated sulphuric acid it yields a magnificent orange colour, and on warming with nitric acid it deflagrates with violence, it also explodes on contact with iodine; its specific rotatory power is $[\alpha]_D = -22{\cdot}5°$, but if heated for some time over metallic sodium, it is reduced to − 0·85°. The author finds that by heating safrole gently with an equal quantity of an aqueous solution of potassium permanganate (1 part in 40 of water) piperonic acid is formed (comp. Abstr., 1884, 1338), and from this and the measurement of the refractive index he considers that the constitution of safrole is probably best expressed by the formula $C_6H_3Pr{<}^{O}_{O}{>}CH_2$ [Pr : $O_2CH_2 = 1 : 3 : 4$] (compare Abstr., 1884, 1339). The residue left after the removal of the above compounds by distillation, when subjected to strong pressure, yields a clear syrup which contains protocatechuic acid, schikimic acid, and schikimipicrin; *schikimic acid*, $C_7H_{10}O_5$, which is present in large quantities, is a white, crystalline compound, insoluble in alcohol, ether, and chloroform, but readily soluble in water, dilute alcohol, and also in concentrated sulphuric acid; it is not precipitated from its solution by metallic salts, and is not affected by ferric chloride, Fehling's solution, or ammoniacal silver solution; an alkaline solution of auric chloride, however, acts on it readily, oxalic acid being formed; bromine also acts violently on its aqueous solution; by fusion with potassium hydroxide, it appears to yield protocatechuic acid. It is a strong acid, readily decomposing carbonates; it melts at about 178—180° (uncorr.), and has a specific rotatory power $[\alpha]_D = -200{\cdot}4°$, its salts are difficult to crystallise, being very soluble in water. *Schikimipicrin* forms large, transparent crystals, readily soluble in warm water or alcohol, but insoluble in ether, chloroform, and light petroleum, it melts at 200° (uncorr.), its reaction is neutral, and it has an extremely bitter taste. A. P.

Analyses of Varieties of Lupines, Beans, and Maize grown under like Conditions. By E. Flechsig (*Landw. Versuchs-Stat.*, **32**, 179—195).—Full tables are given, showing the analytical results obtained with 10 varieties of lupines, 12 varieties of beans, and 9 varieties of maize, grown under identical conditions as regards soil, manuring, &c.

Nitrogenous Organic Compounds in the Soil. By G. Loges (*Landw. Versuchs-Stat.*, 1885, 201—202).—Hydrochloric acid extracts from the soil, besides humic acid, a nitrogenous compound. This compound could not be separated by dialysis, but it forms a voluminous, yellow precipitate with phosphotungstic acid. The composition of this humic substance is still uncertain; samples prepared from two kinds of soils contained N = 6·8 and 6·5 per cent., C = 45·4 and 37·3 per cent. E. W. P.

Analytical Chemistry.

Apparatus for the Quick Reduction of Measured Gas Volumes to Normal Condition. By C. Winkler (*Ber.*, **18**, 2533—2535).—A modification of Kreusler's apparatus (Abstr., 1884, 775).

New Arrangement of the Volumetric System. By C. Winkler (*Ber.*, **18**, 2527—2533).—The author thinks that the volumetric system should be derived from the molecular weights, and not from the equivalent weights, as is the case at present.

A Method of Filtration by Means of easily soluble and easily volatile Filters. By F. A. Gooch (*Amer. Chem. J.*, **7**, 87—90).—Anthracene is proposed as a substitute for asbestos for filtering in cases where the use of paper is objectionable. The anthracene is moistened with alcohol, then mixed with water, and applied to a perforated cone or crucible in the same way as asbestos. If necessary, a finer coating, made by dissolving anthracene in hot alcohol and precipitating by water, is afterwards added. After filtration, the anthracene may be removed by treating in a small beaker with warm benzene; on adding water the benzene solution rises, and may be removed by filtration through a wet filter-paper if thought necessary. The anthracene may also be removed by gentle heating. H. B.

Estimation of Water of Crystallisation in Organic Compounds. By E. Ostermayer (*Chem. Centr.*, 1885, 603—604).—The method described by the author is one employed to estimate the amount of water in the salts of iodonaphtholsulphonic acid, which, like many other organic compounds, loses iodine on heating. A weighed quantity of the salt is heated in a current of dry air in a tube placed in an oil-bath at 110—120°; the tube is connected with one containing a silver spiral, and this with a chloride of calcium tube. The silver is gently heated, and combines with the iodine given off, whilst the water is collected by the calcium chloride, the increase in weight of the latter giving the amount of water. P. P. B.

Diphenylamine as a Reagent for Free Chlorine. By H. Hager (*Chem. Centr.*, 1885, 588).—As a very delicate test for traces

of free chlorine, the author uses a solution of diphenylamine in strong sulphuric acid, poured gently down the side of the vessel containing the liquid to be tested. Should no blue coloration be formed, even after standing for a few minutes with subsequent agitation, a small quantity of pure concentrated sulphuric acid should be added, when even very small traces of free chlorine will show themselves by a blue ring forming at the junction of the two liquids. J. K. C.

Naphthol as a Reagent for Free Chlorine and Bromine. By H. Hager (*Chem. Centr.*, 1885, 692—693).—A 1 per cent. alcoholic solution is used; about 0·5 c.c. of this is poured gently into a narrow cylinder containing 4—5 c.c. of the liquid to be tested. After standing for a few minutes, traces of free chlorine or bromine are shown by the formation of a milky ring where the two liquids meet. Nitric acid and ferric chloride should be well diluted before applying the test. J. K. C.

Estimation of Iodine. By G. Weiss (*Chem. Centr.*, 1885, 634, and 712—713).—The author has lately received samples of iodine, which, when estimated by the ordinary method of titration with hyposulphite, gave over 100 per cent. of iodine. This was found to be due to the presence of about 3 per cent. of bromine, an impurity due to the fact that the iodine was obtained from the last mother-liquors in the preparation of nitre, by precipitation as cuprous iodide. The greasy nature of this precipitate renders the complete washing out of the chlorides and bromides present exceedingly uncertain.

The author describes a simple method for the quantitative separation of iodine, bromine, and chlorine. The halogens must be present in the form of simple and easily decomposable metallic compounds. Concentrated ferric sulphate solution is added and the whole boiled, when the following reaction takes place: $Fe_2(SO_4)_3 + 2KI = 2FeSO_4 + K_2SO_4 + I_2$. During the heating, a current of air is passed through the solution, and then into a solution of potassium iodide. When all the iodine has been carried over into this latter, it is removed for titration and replaced by dilute ammonia. After the residue in the decomposing flask has cooled, a slight excess of potassium permanganate is added to it, and the flask warmed to 50—60°. Evolution of bromine soon commences, and the latter is carried over into the ammonia by the current of air, and then estimated gravimetrically or by titration. The chlorine can be estimated in the residue, or better, by difference, from a determination of the total quantity of iodine, bromine, and chlorine present in the original substance.

If the halogens are present as oxy-acids, they must be reduced by sulphuretted hydrogen or other suitable means; if in the free state they are best converted into zinc iodide by treatment with zinc-dust. L. T. T.

Detection and Determination of Fluorine. By G. Tammann (*Zeit. anal. Chem.*, **24**, 328—343).—Fresenius' method (*Zeit. anal. Chem.*, **5**, 190) of absorbing the silicon fluoride by water and weighing gives good results. For destroying admixed carbonates, evaporation with potash-alum is as effective as boiling with acetic acid. Sulphurous

anhydride may be arrested by a tube containing chromic acid dissolved in strong sulphuric acid. This does not retain silicon fluoride; whereas solutions of potassium dichromate and permanganate in sulphuric acid, and peroxide of lead as proposed by Kupfer, all absorb the fluoride.

In substances free from boron, fluorine may be detected by heating with quartz powder and sulphuric acid at 170° in a stream of air, which is then passed through water. As little as 0·0002 gram of fluorine yields a ring of silica in the wetted part of the tube. The water will then contain hydrofluosilicic acid, besides silica, sulphuric acid and a trace of sulphurous acid. Hydrofluosilicic acid is best precipitated by an alcoholic solution of barium bromide or acetate. Barium silicofluoride can be completely washed with 50 per cent. alcohol, 1 litre of which dissolves 0·0257 gram of it. If evaporation be required, the acetate must be used, since acetic acid does not expel hydrofluosilicic acid, whilst hydrobromic acid does. The acetate should be strongly acidified, and the residue must be treated with hydrobromic acid, to reconvert into silicofluoride any barium fluoride which may have been formed. It is then washed with 75 per cent. alcohol, converted into sulphate and weighed. Test analyses showed that even in highly dilute solutions, the fluorine can be thus determined without serious loss. Soluble fluorides can be analysed in similar manner after conversion into silicofluorides by addition of hydrobromic acid and silica. The excess of silica is removed by hydrofluoric acid after the washing with alcohol.

Barium silicofluoride may be separated from the sulphate by igniting the mixture, and extracting the fluoride of barium by hydrochloric acid.

Attempts to determine fluorine in fluorspar and cryolite by the above processes gave very low results, owing to the fact observed by Landolt, that the action of moist air on silicon fluoride produces an insoluble compound containing fluorine (5—12 per cent.). This body is not decomposed by evaporation with baryta, but is easily soluble in potash. This led to the following method, which gave good results. To the water in which the silicon fluoride has been absorbed, an excess of potash is added, and the whole evaporated to dryness. The residue is treated with hydrochloric acid, and excess of potassium acetate added. It is then mixed with 3 vols. of 80 per cent. alcohol, and the precipitated potassium silicofluoride titrated with potash (Stolba). The same process may be applied without distillation to soluble fluorides, adding silica before the acid, but with fluorspar, &c., distillation is necessary.

Lastly, the author condemns Wilson's method for estimating fluorine in organic compounds, and shows that a loss of from 7 to as much as 68 per cent. of the fluorine may take place during the incineration alone, even when much sodium carbonate or baryta is added.

M. J. S.

Estimation of Carbon in Iron and Steel. By W. Gintl (*Dingl. polyt. J.*, **257**, 527).—The estimation of carbon in iron, according to Wöhler's method—heating in a current of chlorine and igniting the residue to convert the carbon into carbonic anhydride—is

said to give low results, owing to the difficulty of obtaining chlorine free from oxygen. The author proposes to wash and dry the gas carefully, and pass it over a layer of red-hot charcoal, previously ignited in a current of chlorine before applying it to Wöhler's method. D. B.

Detection of Thiosulphates in Water. By G. NEUHÖFFER (*Chem. Centr.*, **16**, 459).—Such impurities are to be found in the water obtained from the neighbourhood of gasworks, and at times from those in the neighbourhood of vineyards. The presence of thiosulphates may be ascertained by adding lead acetate to a litre of the water, collecting the precipitate, washing, and boiling it with sodium carbonate solution. The filtrate is evaporated to dryness, and the residue is tested for thiosulphates by treating it with hydrochloric acid and pure zinc. P. P. B.

Ferrous Ammonium Sulphate as a Reagent for Nitric Acid. By A. ROSA (*Gazzetta*, **15**, 295—296).—Ferrous ammonium sulphate is a delicate reagent for the presence of nitric acid; it is much more sensitive than ferrous sulphate (compare Abstr., 1884, 493). V. H. V.

Diphenylamine and Crystallised Phenol as Reagents for Nitrates and Nitrites. By H. HAGER (*Chem. Centr.*, 1885, 586—588).—As stock solution, 1 gram of diphenylamine is dissolved in 30 c.c. of absolute alcohol and mixed with four or five times its bulk of pure concentrated sulphuric acid. The liquid to be tested is poured into a test-tube, and the diphenylamine solution allowed to run gently down the side: nitric or nitrous acid in the strength of one drop of a 30 per cent. solution to 60 c.c. of water is easily detected by this test, a blue coloration being formed at the point of contact of the two liquids. The absence of all other oxidizing or reducing substances must of course be first ascertained. That the blue coloration is not due to chlorine may be ascertained by a control experiment with crystallised phenol in hydrochloric acid: the liquid to be tested is mixed with this in a test-tube, and sulphuric acid poured gently down the side: a red coloration is formed by the presence of nitrogen acids. J. K. C.

Naphthol and Sulphuric Acid as a Reagent for Nitric and Nitrous Acids and Free Chlorine. By H. HAGER (*Chem. Centr.*, 1885, 693—694).—Mix the liquid to be tested with half its bulk of a 1 per cent. alcoholic naphthol solution, and pour sulphuric acid gently down the side of the vessel: a brownish-red coloration denotes the presence of nitrogen acids or free chlorine: if no ring is formed, shake up, allow to stand for a few minutes, and pour in gently pure concentrated sulphuric acid. J. K. C.

Arsenic in Bleaching Powder and in Potassium Chlorate. By L. GARNIER (*J. Pharm.* [5], **11**, 9).—In 1881, Schlagdenhauffen and the author detected the presence of arsenic in certain samples of

bleaching powder. The author reports that recently potassium chlorate, intended to be used in Fresenius and Babo's method of arsenic estimation in organic matter, was found to contain decided traces of arsenic. The presence of the metal is ascribed to impurity in the chlorine employed in manufacturing the salt. J. T.

Estimation of Arsenic in Ores, Mattes and Metallic Copper. By G. W. Lehmann and W. Mager (*Amer. Chem. J.*, **7**, 112—113).—R. Pearce's method (*Engin. Min. J.*, 1883, 256) is found to be the most trustworthy and convenient. The material is fused with nitre and sodium carbonate, and the filtered solution acidified with nitric acid and boiled. Silver nitrate and ammonia are added, the precipitate of silver arsenate is washed, and the silver in it estimated by Volhard's method. Metallic copper must be dissolved in nitric acid, and the arsenic precipitated as ferric arsenate by addition of a ferric salt and ammonia in excess; the precipitate obtained is treated as above. Satisfactory test analyses are given. H. B.

Swedish Method of Testing for Arsenic. By A. Atterberg (*Chem. Centr.*, **16**, 600—602).—A small portion of the substance is treated in a test-tube with dilute hydrochloric acid, zinc and ferrous sulphate. A plug of cotton-wool moistened with lead acetate is placed above the mixture, and in the mouth of the test-tube are suspended two strips of paper moistened with lead acetate and silver nitrate respectively. If the silver nitrate remains unaltered after 12 hours, the substance is declared free from arsenic. If arsenic is found by the above method, then the substance is distilled with hydrochloric acid and ferrous sulphate. A portion of the distillate is tested for arsenic as above, and in another portion, the arsenic is precipitated as sulphide, and metallic arsenic obtained from the sulphide by reduction with potassium cyanide and sodium carbonate in a current of carbonic anhydride; the density of the arsenic mirror determining the condemnation, or otherwise, of the goods. The author proposes to evaporate the distillate with nitric acid: the arsenic is then obtained in the form of arsenic acid, the presence of which can be easily recognised by the characteristic reaction with silver nitrate. P. P. B.

Eyster's Scheme for Qualitative Analysis. By R. B. Warder (*Amer. Chem. J.*, **7**, 110—112). Eyster's scheme is described in *Amer. Chem. J.*, **7**, 21—26; a modification is here proposed for the detection of cadmium, copper, nickel, and cobalt: the cadmium is precipitated by ammonium sulphide in presence of potassium cyanide; addition of acetic acid to the filtrate throws down the copper as sulphide, and on adding hydrochloric acid to the filtrate from this, nickel is precipitated as sulphide, whilst the cobalt remains in solution. H. B.

Separation of Iron and Aluminium. By M. Ilinski and G. v. Knorre (*Ber.*, **18**, 2728—2734).—The metals must be present as sulphates or chlorides, as in the case of nickel and cobalt (this vol., p. 840). The very slightly acid solution is treated with an equal volume of 50 per cent. acetic acid, and an excess of nitroso-β-naphthol (dis-

solved in 50 per cent. acetic acid), and the whole stirred. After 6—8 hours it is filtered, and the precipitated ferrinitrosonaphthol washed, first with cold 50 per cent. acetic acid, then with water, dried, ignited with pure oxalic acid, and weighed as Fe_2O_3.

Ferrinitroso-β-naphthol, $(C_{10}H_6O{\cdot}NO)_3Fe$, forms a voluminous brownish-black precipitate, soluble in warm moderately dilute hydrochloric or sulphuric acid; it is also soluble in glacial acetic acid and in alcohol. Benzene, aniline, and phenol dissolve it with formation of dark-brown solutions. Warm concentrated potash solution decomposes it with formation of ferric hydroxide and a green potassium salt of nitrosonaphthol.

Ferronitroso-β-naphthol is formed when a very dilute solution of a ferrous salt is treated with an aqueous solution of nitroso-naphthol: the solution becomes green, and after a long time a separation of green flakes of ferronitrosonaphthol takes place. This compound is very susceptible towards free mineral acids, and is therefore not formed in a strong solution of ferrous sulphate. N. H. M.

Estimation of Manganese. By Diehl (*Chem. Centr.*, 1885, 713—714).—The author previously recommended the estimation of manganese in the presence of iron by precipitation of the mixed oxides, Fe_2O_3 and MnO_2, by hydrogen peroxide, conversion of these by ignition into Mn_3O_4 and Fe_2O_3, and estimation of the iron by titration and of the manganese by difference. He now finds that unless carbonates or organic salts of the fixed alkalis are present, the old method of precipitation of the mixed oxides, Mn_3O_4 and Fe_2O_3, by bromine and ammonia, is as quick, and more exact. L. T. T.

Volumetric Estimation of Manganese by Means of Potassium Chlorate. By W. Hampe (*Chem. Centr.*, 1885, 714—715).—It is well known that potassium chlorate precipitates manganese as peroxide from a boiling solution in concentrated (1·4) nitric acid. The author employs this process in the estimation of manganese in alloys of manganese and iron, &c. The alloy is dissolved in boiling nitric acid, the peroxide precipitated, collected, and titrated. The results are very good. The process may also be used for the estimation of manganese in ores, &c. The presence of cobalt, lead, and bismuth is injurious, and necessitates a re-solution and second precipitation of the peroxide. Sulphuric and hydrochloric acids, if present, must be removed by barium nitrate or by boiling with nitric acid respectively. L. T. T.

Assay of Nickel Coins. By W. C. Roberts (*Pharm. J. Trans.* [3], **15**, 1072).—Half a gram of the alloy is dissolved in a small quantity of nitric acid, 1·5 gram of strong sulphuric acid is added, and the whole evaporated to dryness. The residue is dissolved, diluted to about 60 c.c., put into a platinum dish which forms the negative electrode of an electric circuit, the positive electrode being a flat platinum spiral suspended in the liquid; the solution should be distinctly acid; two pint "gravity" cells are sufficient for the deposition of the copper, which is complete in 12 hours, when the copper is washed, &c.

The solution and washings are heated, made ammoniacal, any precipitated iron removed, and evaporated to about 60 c.c., the solution is then put into a platinum dish, and electrolysed, using three cells; the nickel is deposited forming a white, coherent layer. Nitrates must not be present except in the smallest possible quantity. D. A. L.

Electrolysis of Molybdenum Solutions. By E. F. Smith and W. S. Hoskinson (*Amer. Chem. J.*, **7**, 90—92).—In a previous paper (*Amer. Chem. J.*, **1**, No. 5) it was shown that molybdenum could be completely separated by electrolysis from alkaline molybdic acid solutions, but only after a lapse of 100 hours. It has since been found that precipitation is complete in two to three hours if the solutions employed are faintly acid or neutral. The dense black deposit is in all cases $Mo_2O_3,3H_2O$, and not metallic molybdenum, as stated in the *Handwörterbuch der Chemie*. A number of very satisfactory test analyses are given. H. B.

Determination of Sulphurous Acid in Beer. By J. Herz (*Chem. Centr.*, 1885, 523).—200 c.c. of the beer are acidified with phosphoric acid, and 100 c.c. distilled over; the amount of sulphurous acid in the distillate is finally determined as barium sulphate. Beer brewed at the Court Brewery gave by this method from 0·00179 to 0·00261 gram SO_2 per litre, whilst 0·00373 gram per litre represents the mean of the results obtained with 84 samples of different beers. In the light of these results, the author would regard as suspicious any beer which, when treated as above, yields a distillate giving from 5—10 mgrms. of barium sulphate, and if above 10 mgrms. of barium sulphate there can be no doubt as to the presence of sulphites.

P. P. B.

Oxidation of Carbohydrates by Means of Chromic Acid. By C. F. Cross and E. J. Bevan (*Chem. News*, **52**, 207—208).—Having observed considerable quantities of carbonic oxide in the gas evolved during the oxidation of cellulose, sugar, &c., by means of a mixture of chromic and sulphuric acids, the authors have resorted for quantitative work to a volumetric method, and have successfully employed a modification of Scheibler's carbonic anhydride apparatus for the purpose. The chromic acid is introduced in a small tube into a small flask connected with the apparatus, and containing the substance mixed with strong sulphuric acid, the levels are adjusted, and then the contents of the flask are mixed by inclining and shaking. The authors intend extending the application of this method.

D. A. L.

Estimation of Uric Acid. By E. Ludwig (*Chem. Centr.*, 1885, 523).—100 c.c. of the urine are treated with magnesia mixture and an ammoniacal solution of silver nitrate; in this way a precipitate of magnesium silver urate and magnesium ammonium phosphate is obtained. The precipitate is digested with a solution of potassium sulphide and filtered, the filtrate contains potassium urate, from which, after concentration, the uric acid is precipitated by hydrochloric acid. The uric acid is collected on a filter of glass-wool, freed from sulphur by washing with carbon bisulphide, dried and weighed. If the urine

contains albumin this must be first removed by boiling with solution of salt and acetic acid, and treating the filtrate as above. The author finds the precipitation of uric acid by hydrochloric acid is never complete, even after several days. P. P. B.

The Detection of Adulteration in Oils. By O. C. S. Carter (*Amer. Chem. J.*, **7**, 92—96).—Cotton-seed oil may be detected when added to olive oil or to lard oil, by adding 5 vols. of absolute alcohol and an equal volume of a 1 per cent. solution of silver nitrate in absolute alcohol; if cotton-seed oil is present, the mixture will rapidly darken on warming to 84°. The presence of much of the drying oils, such as linseed, hemp-seed, or poppy-seed oil, is shown by treatment with nitrogen peroxide; they do not solidify from formation of elaïdin. The ease and completeness with which an oil may be saponified is a valuable test; lard oil saponifies easily; shark-liver oil and African fish oil resist saponification. H. B.

Detection of Fat Oils in Mineral Oils. By F. Lux (*Zeit. anal. Chem.*, **24**, 357—362).—When colza oil is heated with potassium, or sodium, or their solid hydroxides, soaps are formed. The higher the temperature, the more rapid is the saponification. Between 200° and 250° the soaps dissolve in the oil, which, on slight cooling, gelatinises or even solidifies (varying with the alkali used). Mineral oils similarly treated do not alter in fluidity. The author tested numerous mixtures of petroleum and lubricating oils with colza, linseed, and olive oils, and found that 2 per cent. of the fat oil in all cases, and $\frac{1}{2}$ per cent. in some, could be detected with certainty by the gelatinisation which occurred on cooling, after 15 minutes' heating at 200° with sodium or solid caustic soda. With less than 2 per cent., it is necessary to heat the test-tube in a paraffin-bath and to avoid agitation during both heating and cooling, but with larger proportions a short boiling over the free flame suffices. M. J. S.

Examination of Oils containing Unsaponifiable Fats. By T. Morawski and H. Demski (*Dingl. polyt. J.*, **258**, 39—42).—For the estimation of unsaponifiable fats in oils, the authors recommend the following method, having special reference to the difficulty experienced in completely separating the saponified oil from the unsaponifiable fat. 10 grams of the oil are treated in a flask with 50 c.c. of alcohol and 5 grams of caustic potash dissolved in a small amount of water. The mixture is boiled for half an hour in a reflux apparatus. The liquid is then diluted with 50 c.c. of water, cooled as rapidly as possible, transferred to a separating funnel, and agitated with light petroleum. The mixture is allowed to settle, the lower layer drawn off, and the petroleum washed repeatedly with water. To remove the last particles of water, the petroleum extract is first poured into a dry flask and then transferred to a tared flask from which the petroleum is expelled by distillation. D. B.

Test for Adulteration in Butter. By A. Wagner (*Chem. Centr.*, 1885, 412—413).—This method depends on the fact that natural

butter forms an emulsion much more easily than other fats. About 0·6 gram of butter is put in a flask with 12 c.c. of water and 2 drops of a 2 per cent. soda solution, and the whole well shaken; it is then heated on a water-bath at 37°, and transferred to a separating funnel, being washed out with water at the same temperature. From time to time, the emulsion is allowed to run out, being replaced with water at 37° until the water becomes quite clear; it is then carefully run out, and after cooling, the walls of the funnel are covered with a finely divided cheese-like mass if pure butter has been operated upon, but the presence of any other fat is made apparent by oily drops which are visible also during the previous process. J. K. C.

Critical and Experimental Study of the Knop-Hüfner Method of determining Urea. By C. Jacobj (*Zeit. anal. Chem.*, **24**, 307—328).—The author defends the hypobromite process against the objections of Arnold (Abstr., 1883, 1141), and maintains that if the operation be carried out in a uniform way, the use of an empirical constant for calculating the nitrogen into urea will always give satisfactory results. Hüfner by using 5 c.c. of a 1 per cent. urea solution and 100 c.c. of Knop's original hypobromite reagent, obtained 354·3 c.c. of nitrogen (at 0° and 760 mm.) from 1 gram of urea. Using this constant, the author made a series of determinations with pure urea solutions, varying in strength from 0·666 to 3·0 per cent. by both the Liebig-Pflüger and the Knop-Hüfner methods, and found that the latter gave on the whole the smaller errors. These were in almost all cases errors of deficit, and the deficiency increased somewhat—though not proportionally—with the strength of the urea solution, whilst Liebig's method gave more irregular results, sometimes much above the truth. With normal urine, and also with that of fever patients, Liebig's method invariably gave higher numbers than Hüfner's, the difference being greatest with the pathological urine. With diabetic urine, containing 3 or 4 per cent. of sugar, Hüfner's method still gave the lower numbers, but with a specimen containing 6 per cent., the use of the constant 354·3 led to a result higher than that yielded by Liebig's process. Determinations by both methods in solutions of pure urea, to which varying quantities of grape-sugar had been added, showed that the amount of nitrogen liberated increases with increasing quantities of sugar, although with as much as 6 per cent. it did not reach its theoretical limit. Substituting for the sugar 1 to 5 per cent. of ethylic acetoacetate (the presence of which in diabetic urine has been suspected), practically the theoretical quantity of nitrogen was obtained, instead of the usual deficiency of 8 per cent., and with healthy urine, to which 1 per cent. of the ether had been added, the use of the theoretical constant 371·4 gave approximately the same results as the use of 354·3 in the absence of the ether. Liebig's method gave higher results, supporting the view that mercuric nitrate precipitates other substances from urine besides urea. The author recommends that 4 per cent. of the ether should be added to diabetic urine, and the constant 371·4 used in the calculation.

Finally it is argued that the results of this method are affected

only to an insignificant extent by the other nitrogenous constituents of urine, except albumin and ammonia salts, of which the former is easily removed, and the latter, even if it be not right to calculate it as urea (which is almost certainly formed in the system by the dehydration of ammonium carbonate), can be determined by Schlösing's or Schmiedeberg's method, and allowed for. M. J. S.

Presence of Glutamine in Sugar-beet. By E. Schulze and E. Bosshard (*Landw. Versuchs-Stat.*, 1885, 129—136).—In a previous communication (Abstr., 1885, 658), the authors have shown that glutamine can be precipitated by means of mercuric nitrate from the juice of sugar-beet; Scheibler has also obtained glutamic acid from beet molasses. In this paper the method employed to precipitate and estimate the glutamine in the crude juice is described; the quantity (1 gram per litre) obtained by this process is far below that which is really present (5·96 grams per litre); the difference is due to the imperfect precipitation, &c. It is this glutamine which, after boiling, is converted into the glutamic acid detected by Scheibler.

E. W. P.

Estimation of Alkaloïds in the Leaves of Atropa Belladonna. By W. R. Dunstan and F. Ransom (*Pharm. J. Trans.* [3], **16**, 237—238).—20 grams of dried and finely-powdered leaves are exhausted with about 100 c.c. of absolute alcohol. The alcoholic liquid is diluted with about an equal volume of water slightly acidified with hydrochloric acid, warmed and extracted with chloroform to remove chlorophyll, fat, &c. The aqueous residue is rendered alkaline with ammonia and again extracted with chloroform. The chloroform solution on evaporation leaves a residue of the pure alkaloïd which is dried at 100° and weighed. Foreign leaves have been found to contain 0·22 per cent. total alkaloïd, and English leaves overheated in drying 0·15 per cent. D. A. L.

Sulpho-conjugate Colouring Matter in Wines. By Carles (*J. Pharm.* [5], **11**, 109—110).—The author finds that the method recommended for the detection of these colouring matters in wine is not generally applicable. It consists in removing sulphates by means of barium chloride, removing the barium salt by means of an alkaline carbonate, then evaporating and calcining the residue; sulphates thus produced are supposed to indicate the artificial colouring matters in question. Erroneous results were obtained not only with wines known to be pure non-plastered, but also with wines made by the author from choice grapes in glass vessels (1) without any addition, (2) plastered with sulphurous gelatin. J. T.

Composition of Long-wool and Merino Fleeces. By W. Chludinsky (*Landw. Versuchs-Stat.*, 1885, 117—128).—The author describes his method of estimating the composition of fleeces, and enters into considerable detail concerning the apparatus (*Eurianalyser*) which he has designed for the removal of the grease by means of carbon bisulphide. As regards the composition of various wools, it is stated that the hygroscopic properties of different wools are almost

identical; merino fleeces have less impurity in them than other fleeces, but are richer in insoluble suint; of other than merinos, Southdown fleeces are most largely contaminated with impurities, whilst the highest percentage of pure wools is found in fleeces from short-tailed sheep. E. W. P.

Diagnosis of Keratin in Animal Tissues. By H. Steinbrügge (*Zeit. Biol.*, **21**, 631—635).—The author has applied Ewald and Kühne's method (*Verh. Med. Vereins z. Heidelberg*, **1**, 451) to the investigation of the tissues of the ear of mammalia for the presence of keratine as a normal constituent, which was a probability to be inferred from the morphological relationship of the tissues to the ectoderm of the ovum. The sections examined were 20 in number, obtained from various sources. They were digested in a trypsin solution prepared in the usual way from pancreas. Very divergent results were obtained in regard to the degree of resistance to the action of this solution, which was the criterion adopted by the authors above mentioned for the presence of *keratin*. Investigation showed that these divergencies corresponded with the degree of action of the hardening solutions employed in preparing the tissues for cutting, and that the criterion in question is worthless. C. F. C.

Technical Chemistry.

Oxalate Developer for Gelatin Plates. By H. W. Lord (*Chem. Centr.*, 1885, 668).—10 grams of sodium sulphite are dissolved in 175 c.c. of a concentrated solution of potassium oxalate and 50 c.c. of a concentrated solution of ferrous sulphate added. About 1 c.c. sulphuric acid is then dropped in, until the mixture smells of sulphurous acid. This forms a very energetic developer, and the same quantity may be used several times. L. T. T.

New Photographic Copying Paper. By H. J. Shawcross (*Chem. Centr.*, 1885, 668).—The author covers the prepared paper with the powdered solid developer (tannic acid or other compound giving coloured precipitates with ferric but none with ferrous salts), which is well rubbed in. After exposure under the drawing to be copied the paper is laid in water, and the excess of developer removed with the aid of a sponge. A separate developing bath is thus avoided. L. T. T.

Electric Accumulators. By S. Schenek and S. Farbaky (*Dingl. polyt. J.*, **257**, 357—369 and 458—465).—In 1883 the Academy of Mining and Forestry in Schemnitz, Hungary was furnished with incandescent lamps, the electric current being supplied by about 90 accumulators. The present paper describes the construction of the accumulators employed, and gives an account of some observations made by the authors. To study the behaviour of the sulphuric

acid during the condensation and the discharge of the current, a series of experiments was made. It was found that when the accumulators are charged the sulphates are decomposed, sulphuric acid being liberated, whilst on discharging, the sulphates are again formed, the free acid being recombined. To determine the ratio of accumulated energy to acid set free, and the ratio of discharged energy to acid fixed, a further series of trials had to be made. The results appear to show that when the accumulators are charged, 2·23 grams of sulphuric acid are liberated per ampère per hour, and that during their discharge 2·25 grams of acid are fixed, giving a mean value of 2·24. The authors term this number the electrochemical equivalent of sulphuric acid for an electric force of one ampère per hour. From this value, some useful data in regard to the preparation, treatment, and application of electric accumulators are said to be derived. D. B.

Selenium Battery. By C. E. Fritts (*Dingl. polyt. J.*, **258**, 44).—The author in conjunction with Hopkinson has patented selenium cells of a certain construction, capable of generating a current of electricity under the action of rays of light. A description of this battery is given in the original paper and more fully in *Engineering*, **39**, 398 (see also this vol., p. 2). D. B.

Gas Analyses. By F. Fischer (*Dingl. polyt. J.* **258**, 28).—Analyses of the gases from regenerative furnaces of the Hasse-Didier type and from pyrites kilns are given. D. B.

Liquid Carbonic Anhydride. By H. Herberts (*Chem. Centr.*, 1885, 543—544, 558—560, and 572).—The author describes in detail the various methods at present employed for the manufacture of this product on the large scale, as well as the objects and uses to which it may be applied. He has patented an apparatus and method for making the gas by the action of sodium bisulphite on a suitable carbonate, and also describes a process for obtaining it from alkaline bicarbonates. He proposes to employ liquid carbonic anhydride as a motive power where fuel is expensive. J. K. C.

Further Experiments on the Decomposition of Ammonium Sulphate by Means of Sodium Sulphate. By G. Blattner (*Dingl. polyt. J.*, **257**, 474—479).—In a previous communication (Abstr., 1885, 613), the author gave an account of some experiments made with the view of testing the correctness of Carey and Hurter's reaction of obtaining ammonia from ammonium sulphate by decomposition with sodium sulphate, the sulphuric acid being utilised simultaneously. These experiments were made without the use of superheated steam, and it was found that from 15 to 18 per cent. of the ammonia originally present in the ammonium sulphate employed was lost by decomposition. The object of the present investigation was to ascertain whether by the use of superheated steam it was possible to avoid the loss of ammonia or to reduce it to a minimum. The results showed that although the loss of ammonia was diminished (to from 1 to 3 per cent.), a large pro-

portion remained in the residue, and sublimed in the form of hydrogen ammonium sulphate, only from 80 to 90 per cent. of the ammonia being liberated as such. The author considers that the success of this process on a large scale depends on the complete removal of these difficulties. D. B.

Treating Celestin and Heavy Spar. By F. Kontheb (*Dingl. polyt. J.*, **258**, 46).—Heavy spar, celestin, or gypsum is introduced into fused sodium or potassium chloride, when the impurities sink to the bottom. The fused mass is then drawn off, cooled, and lixiviated with water, the object being to obtain the sulphates in a finely divided state suitable for further chemical treatment (with sodium carbonate, ammonium carbonate, &c.). The resulting mass may be used also as a pigment for stucco-work, &c. D. B.

Treating Raw Phosphates. By P. Dietrich (*Dingl. polyt. J.*, **257**, 484).—Crude phosphates containing calcium oxide or carbonate are treated with sulphurous anhydride to form gypsum, so that by the subsequent treatment with dilute acids only the phosphate is attacked. To effect the complete conversion of the calcium oxide into gypsum, a mixture of air and sulphurous anhydride is allowed to act on the phosphate in the presence of superheated steam.

D. B.

Preparation of Alumina. By G. Rosenthal (*Dingl. polyt. J.*, **257**, 539).—On evaporating a solution of aluminium sulphate and magnesium chloride, alumina, magnesium sulphate, and hydrochloric acid are obtained. The residue is mixed with a small amount of caustic lime, and subjected to the action of superheated steam at 300°. After lixiviation, alumina mixed with ferric oxide remains. Owing to the higher specific gravity of the latter, its separation from the alumina may be effected by elutriation. D. B.

Preparation of Chromic Acid. By W. A. Rowell (*Dingl. polyt. J.*, **258**, 47).—It is proposed to treat the solution of a chromate with a soluble strontium salt, a precipitate of strontium chromate being obtained. The filtrate, containing some strontium chromate in solution, is treated with barium chloride. The barium chromate thus formed is decomposed with hot dilute sulphuric acid in large excess. The mixture of dilute chromic and sulphuric acids having been separated from barium sulphate is treated hot with an amount of strontium chromate equivalent to the sulphuric acid present. This results in the formation of chromic acid, which is separated from the precipitate of strontium sulphate and evaporated to dryness.

D. B.

Irregularities in the Composition of Steel Ingots. By P. Zetsche (*Dingl. polyt. J.*, **258**, 21).—From an examination of the composition of different sections of steel ingots, the author infers that the metalloïds sulphur and phosphorus predominate in the inner parts of the castings, whilst silicon and manganese are found mainly in the outer portions. D. B.

Improvements in Metallurgy. (*Dingl. polyt. J.*, 258, 31—39.)—To work up tin scrap, Lambotte proposes subjecting the metal to the action of dilute gaseous chlorine at a temperature exceeding the boiling point of chloride of tin. The vapours of stannic chloride evolved are condensed in chambers or passed into a solution of stannic chloride.

For the production of an alloy of high conductivity Shaw mixes 100 parts of copper with 1 to 5 parts of aluminium, and adds 0·05 to 1 part of phosphorus. The aluminium previously mixed with palm oil is gradually stirred into the fused copper. The phosphorus is then introduced, and the mass poured into flat moulds.

Guillemin prepares alloys of copper and cobalt of great firmness and tenacity by fusing copper and cobalt with boric acid and charcoal. The tensile strength of the resulting alloy amounted to 40 kilos. per square mm. It contained 48·3 per cent. of cobalt, 50·3 per cent. of copper, 1 per cent. of nickel, and 0·4 per cent. of iron.

According to Crooke molten lead does not take up the silver, arsenic, and antimony from copper ores unless it is mixed intimately with the ore at a temperature below the fusing point of copper.

In precipitating copper from sulphate solutions by electrolysis, using insoluble anodes, Hartmann prevents polarisation by saturating the solution with sulphurous anhydride and heating it. The electrolytic purification of copper is discussed in detail by Kiliani in the original paper (see also Bergund, *Hütt. Zeit.*, 1885, 249). D. B.

Demercurising Gold. By B. Fischer (*Chem. Centr.*, 1885, 447).—The gold is rubbed well with a paste of powdered iodine and alcohol, and then placed in strong potassium iodide solution. This process is repeated until all the mercury is dissolved, and the gold is then polished with whiting. J. K. C.

Electrolytic Extraction of Gold. By H. R. Cassell (*Chem. Centr.*, 1885, 623—624 and 637—638).—The author employs nascent chlorine, liberated from a chloride of sodium solution by electrolysis, as a solvent for the gold to be extracted. The chlorine appears to have a selective affinity for the gold, gold chloride being formed before any of the other metals present are acted on. The solution must be kept alkaline by the addition of slaked lime, as otherwise the hydrochloric acid which is always formed by the electrolytic process, acts on the iron present in the ore to form ferrous chloride, which at once precipitates the gold that has gone into solution. As long as excess of lime is present, no ferrous chloride is formed.

The apparatus employed consists of a vertical cylinder about 3 feet long and 4 feet in diameter, revolving in a wooden vat. The cylinder is isolated from the vat, and has its surface of porous material. The positive wire from the dynamo passes into the cylinder and terminates in a number of thick carbon rods, the negative wire ends in the vat, in a roll of copper foil. Both vat and cylinder are charged with a strong solution of salt, and the dynamo started. The pulverised ore is then gradually introduced into the upper end of the cylinder (which is given about ten revolutions per minute) so that in falling

it comes in contact with the positive poles of the battery. The process takes about four hours for completion. The solution containing all the gold can then be decanted or filtered off, and the gold precipitated by iron or other suitable substance. If the surface of the cylinder is covered with asbestos cloth, or other suitable filtering material, the gold chloride passes through, and the gold is then precipitated as a black powder at the copper negative pole, and may be collected and melted. This latter plan is the best in general practice.

L. T. T.

Solubility of Mercuric Iodide in Fatty Compounds and other Solvents. By C. Méhu (*J. Pharm.* [5], **11**, 249—255).—*Oil of sweet almonds* heated on a steam-bath dissolves about 13 parts of iodide per 1000 of oil, but on cooling about two-thirds of this is deposited. Heated at 180°, about 80 parts iodide per 1000 parts oil are dissolved, but a considerable proportion is deposited at 150° in yellow crystals, which rapidly pass into the red modification on the filter. About 4 parts per 1000 may be considered as the amount retained in the cold. This amount can be increased by the addition of potassium iodide.

Olive oil behaves in much the same manner as oil of sweet almonds.

White oil at 100° dissolves 15·35 parts of iodide per 1000. A solution of 10 parts per 1000 remained quite clear when kept for six days in a cellar.

Nut oil at 100° dissolves about 15 parts per 1000, and retains 13 parts in the cold.

Castor oil is one of the most powerful solvents for mercuric iodide. About 40 parts per 1000 are dissolved at 100°. About 20 parts are retained on cooling. A mixture of 80 parts iodide with 48 parts mercuric chloride is dissolved in 1000 parts of oil on the steam-bath, and on cooling only a small quantity of the mixture separates out. About 100 parts of a mixture of equal equivalents of the iodide and chloride are almost completely retained in solution by 1000 parts of oil. Potassium iodide largely increases the solubility of the iodide.

Lard retains about 4·5 parts iodide per 1000 in the cold.

Vaseline dissolves only about 0·25 part per 1000.

Phenol retains less than 10 parts per 1000.

Benzene dissolves 20 grams at 100°, but retains only 4 parts per 1000 in the cold.

The author has experimented with mercury benzoate and other compounds, with a view to obtaining oils containing metallic compounds, but the results obtained with mercuric iodide appear most valuable.

J. T.

Preparation of Ferrocyanides. By A. Sternberg (*Dingl. polyt. J.*, **257**, 539).—The author has found that the sulphur contained in the thiocyanogen-group CNS is readily given up to a metal if the latter can form ferrocyanides simultaneously. The thiocyanate to be treated is mixed with twice the weight of iron filings required to form iron sulphide, and twice the amount of freshly precipitated ferrous hydroxide required to form ferrocyanide. The mixture is agitated in a closed vessel at 110—120°. After twelve hours' digestion about

80 per cent. of the thiocyanate will have been converted into Prussian blue and ferrocyanide. D. B.

Improvements in the Manufacture of Sugar. (*Dingl. polyt. J.*, **257**, 372—378 and 420—431).—It is stated by Koch that on storing beet highly manured with nitrogen, it loses much saccharine matter.

Van Hennekeler has recently tried Despeissis' process of refining sugar by electrolytic means. He found that the mineral constituents pass from the positive to the negative pole, and that the amount of cane-sugar at the positive pole is augmented. Landolt has attempted the destruction of the colouring matters in beet juice by electricity, but has been unsuccessful.

In discussing the processes used for refining beet-juice, Degener observed that for the treatment of bad roots the sulphurous acid process was indispensable, on account of the antiseptic properties of this acid. Although, according to Bergmann, it is more economical and less troublesome to refine without animal charcoal, the quantity of sugar yielded is largely affected. Experiments conducted at the Dahmen Sugar Works proved that with the use of animal charcoal it was possible to obtain about 8 per cent. more sugar, as against a saving in working expenses of 6 pfennigs per 100 kilos. of beet realised when animal charcoal was not employed.

According to Frost, an important element in the success of the defecation process is the use of lime in a finely divided state, and its freedom from grit.

Steffen recommends heating the waste liquors and removing the last portions of calcium saccharate by hot filtration. The latter may then be added to fresh molasses, or washed with hot water and mixed with calcium saccharate from preceding operations.

Bodenbender, in referring to the determination of invert sugar, an operation of some importance as it is required by the English market, observed that other substances present in beet affect copper solutions in a manner similar to invert sugar. To obtain results approaching nearer to accuracy, it is suggested that the sugar under treatment should be titrated with Fehling's solution before and after boiling with caustic soda.

The use of Schmidt and Hansch's polarisation apparatus is recommended by Sickel. Landolt doubts the accuracy of plates of quartz, and expresses the opinion that more trustworthy results are obtained when polarising apparatus are tested with saccharine solutions of definite composition.

Kleemann proposes the use of pulverised lignite for the purification of saccharine juices.

Degener has made a series of experiments with the object of studying the influence of lead acetate on the optical behaviour of certain nonsaccharine substances present in beet-juice. He finds that lead acetate converts the lævo-rotation of asparagine into a dextrogyrate action. The lævo-rotation of the potassium salt undergoes a similar change when an excess of lead acetate is used. Alcohol increases the rotary power of this salt. Glutamic acid is dextro-

rotary, and insoluble in alcohol. Its potassium salt is soluble in alcohol. Lead acetate imparts to glutamic acid a lævorotary action. Malic acid is lævorotary, its optical power however depends on the concentration and alkalinity of its solutions. Alcoholic solutions are optically inactive. The malates are insoluble in alcohol, but in the presence of a large excess of lead acetate a lævorotary action is obtained. Arabic acid, if present in small quantities, does not affect the polarisation of saccharine juices. Tartaric acid is optically inactive. Caustic alkalis or carbonates impart to saccharose a lævorotary action. Lead acetate first decreases the dextrorotary power of saccharose, and finally changes it to lævo-rotation. Aqueous solutions of albumin are not precipitated by lead acetate. In spite of these reactions Degener concludes that the degree of accuracy obtainable with the methods involving the use of alcohol and lead acetate is infinitely greater than that obtained by the use of other processes hitherto recommended. It is necessary, however, to adhere strictly to the conditions as to the proportion of alcohol and sugar (3 vols. to 1 vol.), and to moderate the quantity of lead acetate employed as much as possible. D. B.

Preparation of Tetrachlorindigo. (*Dingl. polyt. J.*, **257**, 212.)—According to the *Badische Anilin und Sodafabrik*, tetrachlorindigo is obtained by treating orthonitrodichlorobenzaldehyde with acetone and caustic soda. A dye is produced which closely resembles indigo. (Compare Abstr., 1884, 1028.) D. B.

Percentage of Water in Different Wood-papers. By B. Lepsius (*Ber.*, **18**, 2491—2492).—In commerce, paper is bought by its "air-dry" weight, and this is taken as the weight at 100° + 12 per cent. added for moisture. The author has examined several papers, and finds that whereas for mechanically-pulped aspen and pine papers (holzschleifstoffen) this is true, for chemically-prepared (soda, or sulphite processes) cellulose papers the addition should only be 10 per cent. L. T. T.

Chemical Products of Putrefaction in their Relation to Disinfection. By B. Sanderson (*Pharm. J. Trans.* [3], **15**, 897—898, 911—912, and 991—992), from the Thirteenth Annual Report of the Local Government Board.

Modification of Siemens' Pyrometer. By J. Spohr (*Dingl. polyt. J.*, **257**, 315).—The author proposes the use of the telephone in the place of the voltameter. D. B.

High Pressure Digesters (Autoclaves) for Chemical Laboratories. By R. Muencke (*Dingl. polyt. J.*, **257**, 283).—The apparatus consists of a cylindrical copper vessel, provided with a cover, which is firmly fastened down by a screw. In order to close the vessel hermetically a leaden ring is placed between the edges of the cover and the vessel. For low tensions (under 25 atmos.) the cover is made of gun-metal or cast iron, whilst for higher tensions phosphor-bronze is employed. The interior of the cylinder may be lined with lead or enamelled as required. D. B.

General and Physical Chemistry.

New Absorption Spectroscope. By M. de Thierry (*Compt. rend.*, **101**, 811—813).—An absorption spectroscope provided with a reflected scale and an eye-piece micrometer, and arranged so that columns of liquid varying in length from 0·1 m. to 10 m. can be examined, the source of illumination being an oxyhydrogen light.

C. H. B.

Electric Conductivity of Serpentine. By E. Wiechert (*Ann. Phys. Chem.* [2], **26**, 336).—The conductivity of serpentine is very variable; the value of its specific resistance in terms of the mercury unit was found to lie between the limits of 20 and 30000 millions; its use as a perfect insulator is thus undesirable.

Marble does not appear to conduct electricity under any observed conditions.

V. H. V.

Coefficient of Conductivity of Electrolytes in very dilute Solutions. By F. Kohlrausch (*Ann. Phys. Chem.* [2], **26**, 161—226).—A few years ago the author in conjunction with Nippoldt determined the coefficient of conductivity for several electrolytes, and showed that these could be arranged in groups, such as the halogen salts of the same metals, the potassium and ammonium salts, the chlorides of the alkaline earths, and the sulphates of magnesium, zinc, and copper. Further, in the case of neutral salts, the values of the temperature coefficients varied within very narrow limits with increase of dilution.

As a general result, curves were drawn in which the proportions of salt in solution were taken as abscissæ, and the coefficients of conductivity as ordinates; the values of the former multiplied by the chemical equivalents are designated the *specific molecular conductivities*.

The researches of Hittorf on the migration of the ions naturally cause an extension of the above researches in the case of very dilute solutions, as offering a possible means for the determination of the mean distance of the molecules.

The method adopted was that of rapidly alternating currents, the results of former observers having shown that in working this method, even when pushed to the most extreme limits, Ohm's law is valid. The molecular proportions or values, m, of electrolytes in unit volume of solutions are understood to be the quantity in grams divided by the molecular weight; such solutions were prepared in which the values for m were varied proportionally from 0·1 to 0·0001. The means adopted for preparing such solutions and their estimation, the determination of their conductivity, the correction for temperature, and other details are described at length in the paper.

A series of tables are given of the coefficients of conductivity, $K_l 10^{10}$, in terms of the mercury unit of such molecular solutions of

various degrees of concentration of ammonium, sodium, lithium, barium, and zinc chlorides, barium, potassium, sodium, and silver nitrates, potassium, sodium, lithium, magnesium, zinc, and copper sulphates, sodium and potassium carbonates, of potassium iodide, chlorate, and acetate, and of nitric, hydrochloric, and sulphuric acids.

Conductivity of Salts.—These determinations show that the conductivity at first varies directly as the molecular proportion, but in the more dilute solutions the value for this ratio gradually diminishes; the former divided by the latter, k/m, is the *specific molecular conductivity* (comp. *supra*). The values for k/m can best be interpreted by considering them as proportional to the relative velocity of the ions under the influence of a constant electromotive force. If then the values for $10^8k/m$ be multiplied by 0·00011, one obtains the velocity in mm./seconds with which the ions pass one another, under the influence of the force of one volt acting through 1 mm. Unequal values are thus obtained, as shown by the following table :—

Kations.	K.	NH_4.	Na.	Li.	Ag.	H.	½Ba.	½Mg.	½Zn.
$w = 10^8k/m \times 0{\cdot}00011$	52	50	32	24	42	272	30	26	20

Anions.	Cl.	I.	NO_3.	ClO_3.	$C_2H_3O_2$.	OH.
$v = 10^8k/m \times 0{\cdot}00011$	84	55	48	42	26	143

It is thus seen that potassium and ammonium, magnesium and zinc, and in dilute solutions SO_4, I, Cl, and NO_3, can be classified together in separate groups, a result in accordance with the experiments of Lenz.

Further, it is shown that the water of crystallisation has no influence on the conductivity of the salts.

Certain experiments of Faraday and Gmelin are also repeated, which tend to show that in the case of very dilute solutions not only the dissolved electrolyte, but also, under certain conditions, the water itself is decomposed. Thus if a trace of ammonium carbonate be added to solutions of magnesium and copper sulphates, a precipitation of the hydroxide of the metal appears generally in a dendritic form.

Bouty's law of equivalents (*Thésis*, Paris, 1885) is examined and not found to be generally valid.

The temperature coefficients of solutions containing $m = 0{\cdot}01$ of the various salts examined were found to be approximately equal.

Conductivity of Alkalis and Acids.—The coefficient of these substances relatively to dilution at first increases, reaches a maximum, and then decreases; the maximum occurs with solutions in which $m = 0{\cdot}006$.

The following results are also mentioned: (1) the specific conductivities of potassium and sodium hydroxides are approximately equal, as also those of the halogen and nitric acid; (2) solutions of ammonia and of phosphoric and acetic acids, are exceedingly bad conductors; (3) the curve representing the conductivity of sulphuric acid shows minimum points of inflexion corresponding with the formation of the monohydrate H_2SO_4,H_2O, the pure acid H_2SO_4, and the anhydride respectively. The temperature coefficients of alkalis and acids, with the exception of sulphuric acid, are also approximately equal.

Researches are also promised on the application of the determinations of conductivity for ascertaining the interaction of acids and bases when in the same solution. V. H. V.

Electrical Conductivity of Mixtures of Ethyl Alcohol and Ether. By E. W. R. Pfeiffer (*Ann. Phys. Chem.* [2], **26**, 226—239). In continuation of the author's researches on the conductivity of organic liquids (Abstr., 1885, 1029), an account is given of determinations of the specific conductivity of mixtures of alcohol and ether as functions (1) of the percentage proportion of the latter, the temperature being constant; and (2) of the temperature, the mixtures being of identical composition.

Firstly. The conductivity of such a mixture decreases at first regularly with increase of proportion of ether, until the liquid contains 75 per cent.; at this point the curve representing conductivity in terms of percentage of ether shows a point of inflexion, and thence approaches more gradually to the axis of the abscissæ, until with pure ether the conductivity cannot be measured. It was observed incidentally that the conductivity of such mixtures, kept at constant temperature, slowly decreases from the moment of mixing until a minimum point is reached after a variable interval of time; from this point, the conductivity again increases. As it is improbable that the mere passage of the current should effect the conductivity, this phenomenon may be due to the chemical action between inevitable impurities in the liquids or between the liquids themselves.

Secondly. The temperature coefficient is negative for mixtures containing less than 24 to 29 per cent. ether, at which point it becomes zero; thence it increases, reaches a maximum with 35 per cent., and then again decreases.

Thus both pure alcohol and ether, as also mixtures of them in certain proportions, resemble metallic conductors as regards the negative value of their temperature coefficient. V. H. V.

Electrolysis of Salts. By A. Renard (*Compt. rend.*, **101**, 747—749).—From the results of experiments with aqueous solutions of various salts containing from 0·0001 to 0·1024 gram-equivalent of the metals in 100 grams of solution, the author concludes (1) that if the solution be sufficiently dilute the quantity of metal precipitated is proportional to the concentration of the solution; (2) that if the same current is passed through several solutions, the quantities of the different metals precipitated are in the ratios of their equivalents; (3) that, according to Faraday's law, the quantity of metal precipitated being proportional to the intensity of the current, the conductivity of all solutions containing equivalent proportions of the different metals is the same, as Bouty has shown by direct experiment. C. H. B.

New Method of Determining the Heat of Combustion of Organic Substances. By D. Diaconoff (*J. Russ. Chem. Soc.*, 1885, 283—284).—The author burns the compound under investigation in admixture with finely powdered asbestos and glycerol; the former

divides the particles of the difficultly combustible substance, and secures its entire combustion, the latter maintains the temperature necessary for combustion. A. T.

Relations between the Heat of Formation of Salts and the Initial Rate of their Formation. By A. Potilitzin (*Ber.*, **18**, 1522—1527).—When silver chloride is shaken in the dark with equally concentrated solutions of metallic bromides for three minutes and then allowed to rest for 25 minutes, varying percentages of silver bromide are obtained according to the metallic bromide used. When these percentages are divided by the heat of formation of silver bromide from the metallic bromide, a constant number is obtained; in this case the number is 11·17. Similar results are obtained if instead of silver chloride and a bromide, equivalent quantities of $AgNO_3$ + RCl + RBr are employed.

Comparisons were also made of the percentages of carbonates formed by the action of alkaline carbonates on the chlorides of the alkaline earths and of the heat of formation. In this case also a constant, namely 14 . 1, was obtained by dividing the percentage by the heat of formation.

In these experiments, dilute solutions must be used; further, the initial rates of formation of different salts can only be compared in the case of reactions which take place under quite similar circumstances. N. H. M.

Air or Hydrogen Thermometer for Low Temperatures. By J. J. Coleman (*J. Soc. Chem. Ind.*, **4**, 43).—This instrument is a constant pressure thermometer, and has been specially constructed for taking low temperatures, say to 300° below zero Fahrenheit. D. B.

New Form of Gas Thermometer. By G. Beilby (*J. Soc. Chem. Ind.*, **4**, 40).—The author has attempted the construction of a compact thermometer on the principle of measuring at known and constant temperature and pressure the gas expelled from a bulb or vessel of unknown temperature. D. B.

Source of Error in Vapour-density Determinations. By W. Alexéeff (*Ber.* **18**, 2898—2906).—In order to explain the discordant results obtained by Meyer and Pond (Abstr., 1885, 1033) on the one hand, and by Menschutkin and Konowalow (Abstr., 1884, 1119) on the other hand, in experiments on the dissociation of tertiary amyl acetate and chloride induced by glass (Abstr., 1884, 1119), the author mentions the fact that the glass used in Russia is much more readily attacked by acids and other reagents than German glass. Experiments are quoted with propyl bromide which show that in a Meyer's apparatus no dissociation takes place at the boiling point of nitrobenzene, whereas 40 per cent. is dissociated at 200°. This latter result can be interpreted by the removal of the traces of hydrobromic acid by the vapour of water produced by a chemical action on the glass. If this interpretation be correct, the amount of dissociation will be greater, the greater the ratio of the glass surface to vapour present, a result

in accordance with the most recent experiments of Menschutkin and Konowalow. V. H. V.

Dissociation of the Hydrate of Hydrogen Bromide. By H. W. B. Roozeboom (*Rec. Trav. Chim.*, **4**, 108—124).—The curve of tensions of the hydrate of hydrogen bromide between the temperatures of − 11·3° and − 15·6° recurves in a negative direction, there being three different tensions of dissociation for a given temperature between these points. At the lower tension at 11·3°, the aqueous solution of the hydrate surrounding the solid reaches such a concentration that it has a composition identical with that of the solid hydrate itself. Van der Waals has already pointed out that when this takes place at a lower temperature than that at which the acid or chlorous product of dissociation is given off in the liquid form, the curve of dissociation tensions will take a negative direction limited by a point whose position depends on the heat of formation of the compound in question; the curve then once more assumes a positive direction, and the tension rises with the temperature in the normal manner. The hydrate of hydrogen chloride (*Rec. Trav. Chim.*, **3**, 94) shows a similar phenomenon, but the length of the recurved portion is much shorter. A. P.

Dissociation of the Hydrates of Sulphurous Anhydride, Chlorine, and Bromine. By H. W. B. Roozeboom (*Rec. Trav. Chim.*, **4**, 65—73).—In continuation of his researches on this subject (*Rec. Trav. Chim.*, **3**, 28—104) the author finds that the curves representing the tensions of dissociation of these compounds at different temperatures, are each broken into three segmental curves having different directions, the points of intersection being coincident with the temperatures at which a change of state takes place in one of the products of dissociation. The main details are given in the following tables :—

I. $SO_2 + 7H_2O$.

Intervals		Products of dissociation.
Of temperature.	Of pressure.	
− 9·5° to − 2·6°	150 mm. to 211 mm.	H_2O solid and SO_2 gaseous
− 2·6 „ + 12·1	211 mm. „ 177 cm.	H_2O liquid and SO_2 „
+ 12·2 „ + 17·1	177 cm. „ 250 atm.	H_2O „ and SO_2 liquid

Points of intersection at − 2·6° and + 12·1°.

II. $Cl_2 + 8H_2O$.

Intervals		Products of dissociation.
Of temperature.	Of pressure.	
− 10° to − 0·24°	156 mm. to 248 mm.	H_2O solid and Cl_2 gaseous
− 0·24° „ + 28·7°	248 mm. to about 6 atm.	H_2O liquid and Cl_2 „
+ 28·7° „ —	6 atm. to —	H_2O „ and Cl_2 liquid

Points of intersection at − 0·24° and + 28·7°.

III. $Br_2 + 10H_2O$.

Intervals		Products of dissociation.
Of temperature.	Of pressure.	
− 10° to − 0·3°	25 mm. to 43 mm.	H_2O solid and Br_2 gaseous
− 0·3° „ + 6·2	43 mm. „ 93 mm.	H_2O liquid and Br_2 „
+ 6·2° „ —	93 mm. „ —	H_2O „ and Br_2 liquid

Points of intersection at − 0·3° and + 6·2°.

A. P.

Air-pump Regulator. By N. v. Klobukow (*Zeit. anal. Chem.*, **24**, 399—402).—A simple apparatus by means of which the reduced pressure obtained by means of a water jet air-pump may be rendered constant within 1·0 cm. at whatever pressure required, and however the rate of flow of the water may vary. A. P.

Inorganic Chemistry.

Chlorine Monoxide. By K. Garzarolli-Thurnlackh and G. Schacherl (*Annalen*, **230**, 273—286).—Chlorine monoxide, prepared by the action of dry chlorine gas on well-dried precipitated mercuric oxide, is a dark brown liquid boiling at 5° under a pressure of 738 mm. The vapour has a yellowish-brown colour; its density at 10° is 43·35. It is not decomposed by exposure to light. It dissolves in water,

forming a yellow solution. When chlorine monoxide is passed over lime, chlorine is evolved and calcium hypochlorite formed. The oxide decomposes with explosive violence when it is brought in contact with organic matter. W. C. W.

Bromine Absorption. By E. J. Mills and J. Muter (*J. Soc. Chem. Ind.*, **4**, 96—98).—In the present paper, the authors have tabulated a series of constants of bromine absorption for most of the important resins, a few elementary substances, and some interesting substances of a different nature. The absorption was effected either in carbon bisulphide or in carbon tetrachloride, and was determined by titration with β-naphthol or sodium thiosulphate and decinormal iodine, or by simple colorimetric comparison. Benzoic, cinnamic, and salicylic acids, camphor, naphthalene, and benzaldehyde gave no absorption in carbon tetrachloride. At 11°, anthracene absorbs in tetrachloride 88·67 per cent. of bromine, corresponding with the ratio $C_{14}H_{10} : Br_2$; at about 17° the absorption corresponds with $C_{14}H_{10} : Br_4$. Of resinous substances, the absorption of shellac is below all other substances of its class. As a rule, but not invariably, the greater the solubility of a gum resin the greater is its bromine absorption. The results with elementary substances are remarkable. Thus, tin-dust gives no absorption of bromine, arsenic absorbs in 12 hours 2·85 per cent., and aluminium in 1 hour 8·97 per cent. of bromine, carbon tetrachloride being used as the solvent. Zinc-dust takes up bromine in the proportion $Zn : Br_2$, and antimony in the proportion $Sb : Br_3$. It has already been shown that aniline dissolved in carbon bisulphide absorbs bromine in the proportion 1 : 2. The authors consider it probable in this case, as in that of the toluidines, that additive and not substitution compounds are formed. The chemical activity of paratoluidine in carbon bisulphide,

$$2C_7H_9N : Br_2,$$

is less than in the case of tetrachloride, but, owing to the formation of yellow bye-products, carbon bisulphide is a better solvent for analytical purposes. Orthotoluidine takes up bromine in the proportion

$$C_7H_9N : Br_2,$$

carbon bisulphide being the solvent. In conclusion, it is shown that if the bromine absorption of mixtures of aniline with paratoluidine is known, the composition of the mixture admits of ready calculation. D. B.

Solubility of Hydrogen Bromide at Different Temperatures and Pressures. By H. W. B. Roozeboom (*Rec. Trav. Chim.*, **4**, 102—107).—Determinations of the solubility of hydrogen bromide under pressures varying from 0 to 760 mm. were made at six temperatures between − 25° and 0°. The results obtained formed similar curves for each temperature, the curves seem to be parabolic. The weight of gas dissolved by one part of water varies between 2·52 parts at − 25°, and 2·2 parts at 0°, both under 760 mm. pressure, to 1·1 parts at any temperature between − 25° and 0° when under 0·2 mm. pressure. A. P.

Action of Nascent Hydrogen in Increasing the Activity of Oxygen. By F. Hoppe-Seyler (*Zeit. physiol. Chem.*, **10**, 36—39).—The author criticises the views put forward on this subject by W. Pfeffer (*Unters. Bot. Inst. Tübingen*, **1**, 636), and by M. Traube (*Ber.*, **16**, 117, 1197), and affirms the accuracy of his own theory (Abstr., 1880, 3).

Reaction between Carbonic Oxide and Steam. By A. Naumann and C. Pistor (*Ber.*, **18**, 2894—2897).—In this paper, experiments are described made with a view of ascertaining the temperature at which carbonic oxide and steam react to form carbonic anhydride and hydrogen. The method consisted in passing carbonic oxide, freed from carbonic anhydride and oxygen, over water heated at 80°, so as to obtain an approximately equimolecular proportion of carbonic oxide and vapour of water. The mixed gases were passed through a porcelain tube the temperature of which was roughly determined by introducing into it certain salts or spirals of various metals; the resultant gas was then analysed by the usual methods. The following results were obtained:—At 560° no reaction took place, at 600° 2 per cent., at 900° 8 per cent., and at 904° 10·5 per cent. of the carbonic oxide was converted into carbonic anhydride.

All the conditions which militate against a reaction between carbonic anhydride and hydrogen are favourable to that between steam and carbonic oxide, inasmuch as such a change would be exothermic (+ 10720 cal.), and the resultant carbonic anhydride is very stable at high temperatures, whilst the steam is readily decomposed into hydrogen and oxygen, the latter of which can burn the carbonic oxide.

V. H. V.

Note by Abstractor.—The author seems to be unaware of, or at least does not mention, the elaborate experiments of Dixon on the chemical interaction alluded to above (Abstr., 1885, 479, and Trans., 1886, 94).

Crystalline Form of Calcium Hydroxide. By S. Glinka (*J. Russ. Chem. Soc.*, 1885, 451—452).—Crystals of the hydroxide, which had separated on the surface of samples of hydraulic cement, were found to belong to the rhombic system, notwithstanding their hexagonal appearance. Gay-Lussac obtained calcium hydroxide in the form of hexagonal plates by evaporating lime-water in a vacuum.

A. T.

Schloesing's Law Concerning the Solubility of Calcium Carbonate in Water containing Carbonic Anhydride. By R. Engel (*Compt. rend.*, **101**, 949—951).—The author has already shown (Abstr., 1885, 484) that the solubility of magnesium carbonate in water saturated with carbonic anhydride, follows Schloesing's law up to a pressure of 6 atmos. Caro's experiments (*Arch. Pharm.* [3], **4**, 145) indicate, however, that the law does not hold for calcium carbonate at pressures higher than that of the atmosphere. The author has therefore investigated the solubility of calcium carbonate at high pressures, the method of experiment being the same as in the case of the magnesium compound. The results obtained show that

Caro's experiments were inexact, and that the solubility of calcium carbonate follows Schloesing's law up to a pressure of 6 atmos., beyond which the experiments were not carried. The value actually found is, however, always slightly less than that calculated by means of Schloesing's formula, and the difference becomes greater the higher the pressure. The author's formula for the solubility of magnesium carbonate, $y = \frac{1}{k}\sqrt[3]{x}$, also holds good for the calcium compound.

Barium carbonate likewise obeys Schloesing's law at high pressures, the results obtained being of the same order as in the case of calcium carbonate. C. H. B.

Normal Magnesium Carbonate. By R. Engel (*Compt. rend.*, **101**, 814—816).—When magnesium potassium hydrogen carbonate, $MgCO_3,KHCO_3 + 4H_2O$, is strongly heated, it melts and yields a normal magnesium potassium carbonate, but if the triple carbonate is gradually and carefully heated up to 150° or even 200°, it does not melt but loses its water of crystallisation and half the carbonic anhydride previously combined with the potassium, and leaves a residue of transparent crystals which retain their original form. These crystals are not a double magnesium potassium carbonate, for if they are treated with water potassium carbonate is dissolved and magnesium carbonate is left in crystals which retain the form of the original crystals.

If the normal magnesium carbonate thus obtained is left in contact with water, it rapidly combines with it with development of heat, forming the pentahydrate if the temperature is below 16°, and the trihydrate if it is above 16°. The anhydrous carbonate even absorbs moisture from the air. It is much more soluble in water than the hydrated carbonates, and its solution gradually deposits crystals of the hydrated salt.

This form of magnesium carbonate is obviously very different in its properties from the natural carbonate, and also from the artificial crystals obtained by Senarmont.

If the mixture of potassium carbonate and magnesium carbonate is heated in an atmosphere saturated with aqueous vapour, water is absorbed and the carbonates combine without fusing to form a hydrated double carbonate which has the same crystalline form as the original compound, but is not transparent and seems to be black. This compound is decomposed by water, but does not yield anhydrous magnesium carbonate, the hydrated carbonate being formed in proportion as the decomposition takes place. The same result is observed when the magnesium potassium hydrogen carbonate is decomposed by water. C. H. B.

Combination of Normal Magnesium Carbonate with Potassium Hydrogen Carbonate. By R. Engel (*Compt. rend.*, **101**, 749—751).—The author has investigated the conditions under which normal magnesium carbonate combines with potassium hydrogen carbonate, and finds that for the same solution of potassium hydrogen carbonate the velocity of the reaction decreases as the

temperature rises. If the temperature remains constant, the velocity increases with the initial concentration of the potassium solution. Combination ceases when it attains a certain limit, which is measured by the concentration of the solution of the potassium salt remaining in contact with excess of magnesium carbonate without combining with it. This limit increases with the temperature, and its variation is given by the formula $y = m + nt + pt^2$, where y is the number of cubic centimetres of standard sulphuric acid required to neutralise the carbonates remaining in solution, and m, n, and f are constants having the values 2·5236, 0·00517, and 0·0031086 respectively.

The product of the combination, $MgCO_3,KHCO_3 + 4H_2O$, is decomposed by water, and the decomposition tends towards a limit which is not identical with the limit of combination, but is always inferior to it by a quantity which is practically the same for all temperatures. C. H. B.

Double Nitrates of Silver and the Alkalis. By A. Ditte (*Compt. rend.*, **101**, 878—881).—When a solution containing silver and potassium nitrates is slowly concentrated, potassium nitrate at first crystallises alone, but as soon as the liquid contains at least 3 mols. of silver nitrate for each mol. of potassium nitrate bulky, transparent, right rhombic prisms are formed. These prisms are highly modified and have the composition $AgNO_3,KNO_3$. This double salt is always formed when a solution of the two nitrates contains so much of the silver salt that both nitrates can crystallise simultaneously. If the double salt is treated with water, the silver nitrate is gradually removed.

Rubidium nitrate yields a strictly analogous double salt, and in all probability cæsium nitrate will behave in the same way.

If a solution of silver and ammonium nitrates is gradually concentrated, the silver salt, being less soluble, crystallises alone, but after a time the double nitrate $AgNO_3,NH_4NO_3$, separates in crystals similar to those of the potassium compound. This double salt is easily obtained whenever the mixed solutions contain an excess of the ammonium salt.

Rose stated that a solution of silver and sodium nitrates containing an excess of the former, first yields crystals of silver nitrate only, and afterwards crystals of the double nitrates $AgNO_3,2NaNO_3$; and $AgNO_3,4NaNO_3$. The author finds that when the silver nitrate is in excess, this salt crystallises alone in its ordinary form, but as soon as sodium nitrate begins to separate also, the two salts crystallise together, and the crystals take the ordinary form of sodium nitrate. Whatever the original composition of the solution, the composition of the crystals and the mother-liquor varies continuously, however, and no definite compounds are formed. From this result it follows that silver nitrate is dimorphous, and that one of its forms is isomorphous with sodium nitrate, but the author has not been able to obtain pure silver nitrate in rhombohedrons.

Lithium nitrate crystallises below 10° in prismatic needles containing $5H_2O$, and if a mixture of silver and lithium nitrates is allowed to crystallise at this temperature, the two salts crystallise

separately. Above 15°, however, lithium nitrate forms anhydrous crystals similar to those of sodium nitrate, and if a solution of silver and lithium nitrates is concentrated at this temperature, the two salts crystallise together in rhombohedrons, but the composition of the crystals and the mother-liquor varies continuously as in the case of sodium nitrate. C. H. B.

Anhydrous Cerium Chloride, and Cerium Silicate. By P. Didier (*Compt. rend.*, **101**, 882—884).—Anhydrous cerium chloride is readily obtained by passing a carefully dried mixture of chlorine and carbonic oxide over cerosoceric oxide contained in a carbon dish. It is somewhat easily fusible, but only slightly volatile, highly deliquescent, and dissolves completely in water with considerable development of heat. Oxygen decomposes it at a dull red heat with liberation of chlorine and formation of cerosoceric oxide. If the cerous chloride is previously mixed with sodium chloride, the cerosoceric oxide forms crystals which seem to belong to the cubic system, and have a metallic lustre and a brilliant red colour if they have been produced at a high temperature. This variety of cerosoceric oxide seems to be identical with the crystals obtained by Grandeau by a different method (Abstr., 1885, 872).

Cerous chloride is also decomposed by steam at a high temperature with formation of cerosoceric oxide and hydrochloric acid; but if a mixture of steam and nitrogen is passed over a fused mixture of cerous and sodium chlorides, the oxychloride $Ce_3O_2Cl_2$ is obtained in iridescent, micaceous scales with a silvery lustre. This compound is formed whenever hydrochloric acid and cerium oxide, or cerous chloride and water, are brought in contact at a high temperature, but if oxygen is also present, cerosoceric oxide is also formed. Cerous oxychloride is easily soluble in dilute acids, and when heated in the air gives off hydrochloric acid, a residue of cerosoceric oxide being left.

When silica and cerous chloride are heated together in a platinum dish in a non-oxidising atmosphere, the greater part of the silicon is volatilised in the form of tetrachloride, and long, colourless needles insoluble in water are left mixed with the excess of cerous chloride. These crystals have the composition $SiO_2,2CeO,2CeCl_2$; they act on polarised light, undergo very little change in contact with water, but oxidise and become brown when exposed to the air. If cerium oxychloride is fused with silica and either sodium or calcium chloride, cerium silicate is obtained in highly modified prisms of sp. gr. 4·9, which act strongly on polarised light, and are more or less rapidly attacked by hydrochloric, nitric, and sulphuric acids, according to the concentration of the acid. This silicate has the composition $SiO_2,2CeO$, and is therefore analogous to peridote. C. H. B.

Lead Tetrachloride. By T. Nikolukine (*J. Russ. Chem. Soc.*, 1885, 207—210).—The author finds that by the action of hydrochloric acid on lead peroxide, the reaction being conducted at a low temperature, lead tetrachloride is formed together with the dichloride. Potassium chloride forms with the tetrachloride a double salt, similar

to that with stannic chloride, soluble in a saturated solution of potassium chloride, lead dichloride being very sparingly soluble therein. With ammonium chloride, the reverse is the case, its double salt with lead tetrachloride being insoluble, and lead dichloride soluble in the saturated solution. Lead tetrachloride is a strong oxidising agent, acting even on platinum; its solutions evolve chlorine after a time, and deposit crystals of the dichloride; when heated, chlorine is rapidly evolved. With caustic alkalis and their carbonates, a dark brown precipitate of lead peroxide is formed. In the action of hydrochloric acid on lead peroxide, a double compound of the acid with the tetrachloride is most probably formed. Lead tetrachloride is decomposed by small quantities of water with evolution of chlorine; with large quantities of water a red-brown coloration of the liquid occurs, apparently due to the formation of lead peroxide. A. T.

Double Salts of Ferric Chloride with other Metallic Chlorides. By G. Neumann (*Ber.*, **18**, 2890—2894).—When a large quantity of ferric chloride is dissolved in hot fuming hydrochloric acid, and to it is added the metallic chloride whose double salt is required, and the liquid filtered, double salts of the general formula $Fe_2Cl_6,4RCl + 2H_2O$ separate out on cooling. These crystallise in the regular system, generally as microscopic octohedra or rhombic dodecahedra. In this paper, such double salts of ferric chloride with potassium, ammonium, rubidium, magnesium, and beryllium chlorides are described.

V. H. V.

Molybdenum Residues. By W. Venator (*Arch. Pharm.* [3], **23**, 713—714).—If the residues contain no iron, sufficient ferric chloride is added to give a brownish-yellow colour to the solution. To separate the phosphoric acid, ammonia is added, the precipitate filtered off, and the filtrate is treated with barium chloride, whereby barium molybdate and sulphate are precipitated. The precipitate is well washed with hot water, and boiled for a long time with an equivalent amount of ammonium sulphate and water, with active agitation. The barium sulphate is filtered off, and the ammonium molybdate crystallised out. The product thus obtained is very pure. J. T.

Crystallised Tin. By H. v. Foullon (*Jahrb. f. Min.*, 1885, **2**, Ref., 266—268).—From a series of measurements, the author concludes that only the following allotropic modifications may be regarded as different:—Grey tin (sp. gr. 5·781 to 5·809); rhombic tin (sp. gr. 6·52 to 6·56); and tetragonal tin (sp. gr. 7·196). The author is doubtful whether the modification described as previously melted tin (sp. gr. 7·2795) differs from the tetragonal modification, as the differences in the sp. gr. of the two are not greater than the differences in the values obtained by different observers with tetragonal tin. These differences are obviously due to the numerous gas inclusions.

B. H. B.

Platinum Silicide. By C. G. Memminger (*Amer. Chem. J.*, 172—175).—Topaz was intensely ignited in a platinum crucible placed in a graphite crucible; at the end of the operation the platinum was

found to be fused, having been converted into a brittle, fusible substance containing 1·61 per cent. of silicon. H. B.

Colour Reaction of Rhodium. By E. Demarçay (*Compt. rend.*, **101**, 951—952).—A neutral or feebly acid solution of ammonium rhodiochloride, if sufficiently concentrated, gives a yellowish precipitate with a slight excess of sodium hypochlorite. If a 20 per cent. solution of acetic acid is added drop by drop to the liquid, with continual agitation, the precipitate dissolves and forms a somewhat intense orange-coloured solution, which rapidly decolorises, deposits a greyish precipitate, and finally acquires an intense sky-blue colour. This colour persists for several hours, and then gradually disappears, but can be reproduced by repeating the same operations with the colourless liquid. The disappearance of the blue coloration is accelerated by the presence of any free nitric or sulphuric acid, or of a large excess of acetic acid, and by a rise of temperature. The sodium hypochlorite solution should be freshly prepared and somewhat concentrated; an excess exerts no injurious effect. It is immaterial whether the rhodium solution be originally yellow or red.

Chlorides of other metals of the platinum group give no reaction with sodium hypochlorite under the same conditions. Small quantities of rhodium can be detected in a mixture if two equal portions of the solution are taken for comparison, and one is diluted with water up to the same bulk as that with which the test is performed. In this way, 0·0001 gram of rhodium can be detected in 3 c.c. of liquid, but the blue colour is very faint, and appears slowly.

With potash, the blue solutions of rhodium give a greenish precipitate which dissolves in acetic acid, with production of a dark-blue solution. C. H. B.

Mineralogical Chemistry.

Occurrence of Millerite in St. Louis. By V. Leonhard (*Jahrb. f. Min.*, 1885, **2**, Ref., 403).—Millerite occurs in large quantities in St. Louis, in cavities 1 inch to 1 foot in diameter, in carboniferous limestone. In these cavities, the following minerals occur:—Calcite, dolomite, fluorspar, blende, *millerite*, anhydrite, gypsum, heavy-spar, strontianite, and pyrites. The latter minerals are formed later than the millerite.

The millerite occurs in various forms: long, thin needles being the purest. These crystals are 6 inches long, 0·03 to 0·05 mm. thick, very elastic, with metallic lustre, and brass-yellow colour. They are hexagonal prisms with rhombohedral termination. The analyses gave on an average 64·45 per cent. of nickel, and 35·55 per cent. of sulphur, with some iron (0·8 to 2·65 per cent.). The sp. gr. of the mineral is 5·028. B. H. B.

Emplectite from Rézbánya. By J. A. Krenner (*Jahrb. f. Min.*, 1885, **2**, Ref., 263—264).—The mineral from Rézbánya, described by Peters as bismuthine, is emplectite. An analysis gave the following results:—

S.	Te.	Bi.	Cu.	Ag.	Pb.	Fe.	Total.
18·61	0·16	63·20	16·84	0·20	1·14	0·11	100·26

corresponding with the formula Cu_2S,Bi_2S_3.

The accompanying mineral, described by Peters as tremolite, is shown by the author to be wollastonite. B. H. B.

Zircon and Titanium Minerals. By H. Thürach (*Jahrb. f. Min.*, 1885, **2**, Ref., 396—401).—In conducting an investigation of the rocks of the Spessart, and their alteration products, the author found zircon and titanium minerals in many of the rocks. He has since extended his researches to the rocks of other districts, and the results of his investigations may be summarised as follows:—

Microscopic zircon is rarely absent in the Archæan and sedimentary rocks. It also occurs in very many eruptive rocks. Its wide distribution in basalts and dolerites was hitherto unknown. Rutile is also contained in almost all Archæan and sedimentary rocks, and in the *débris* from granites, porphyries, diabases, basalts, and dolerites. Microscopic anastase is widely distributed in decomposed crystalline and sedimentary rocks, and, in these, occurs principally in two types, one formed by the primary pyramid and the basal plane, and developed in a tabular or pyramidal manner; whilst the other is formed by an obtuse pyramid of the second order and the basal plane, presenting crystals of a lenticular character. Microscopic brookite is distributed in the same way as anatase, and appears in thin or thick tablets with the macrodiagonals predominating, and showing the subordinate planes ∞P, $\breve{P}2$, $2\breve{P}\infty$, $0P$, $\frac{1}{2}P$, $\frac{1}{2}\breve{P}\infty$, and $\infty\breve{P}\infty$. Anatase and brookite never occur in unaltered crystalline rocks, but only when the rock weathers. In the sedimentary rocks, they are partially of recent formation, partially derived from secondary deposits. Pseudo-brookite occurs in the altered basalt and phonolite of the Kreuzberg, and has been formed during the weathering of the rock. Of all the minerals occurring in the sedimentary rocks, staurolite deserves special attention as evidence of the derivation of these rocks from the various Archæan rocks. (Compare Sandberger, this vol., p. 24.)

B. H. B.

Minerals from Switzerland. By G. Seligmann (*Jahrb. f. Min.*, 1885, **2**, Ref., 240—242).—The author describes the following minerals:—Brookite from the Maderana Thal; milarite and turnerite from the Strim Glacier; danburite crystals from the Scopi; topaz, vesuvian and diopside from the Piz Rondadura; iron glance and phenacite from the Bächi Thal. A new occurrence of iron glance, $0R$, $\infty P2$, ∞P, $\frac{4}{3}P2$, R, with adularia, calcite, and quartz, occasionally in very fine twin crystals, is described, from the Gorpibach, a tributary of the Rhône. B. H. B.

Richellite. By G. Cesáro (*Jahrb. f. Min.*, 1885, **2**, Ref., 260).—The results of the analyses are: (I) for compact richellite; (II) for laminated richellite:—

	Hygroscopic H_2O.	H_2O.	HF.	P_2O_5.	Fe_2O_3.	CaO.	Al_2O_3.	Total.
I.	6·90	25·64	1·22	27·23	29·63	6·18	2·82	99·62
II.	9·47	23·63	0·96	25·49	29·67	7·19	3·64	100·05

corresponding with the formula:

$$4Fe_2(PO_4)_2 + Fe_2O_3,2HF + 36H_2O.$$

Richellite is amorphous. It is found in the neighbourhood of Vise (comp. Abstr., 1884, 1102). B. H. B.

Optical Properties of Berzeliite. By Bertrand (*Jahrb. f. Min.*, 1885, **2**, Ref., 246—247).—The author has determined the optical properties of the berzeliite, recently discovered by Igelström (this vol., p. 25) in Nordmark. An examination of the Långban berzeliite conducted at the same time showed that the two minerals differ considerably. The berzeliite from Långbau, which occurs in large fragments, exhibits, on the same specimen, points with single and double refraction; but the double refraction is indistinct, and in convergent light the interference figures cannot be detected. The berzeliite from Nordmark, which occurs almost without exception in round grains without crystal planes, always exhibits distinct double refraction of a very constant character. It is biaxial: $2E = 140°$. The bisectrix is positive; ρ is less than v. As also no dispersion of the axes of elasticity was observed, the author is inclined to regard the Nordmark berzeliite as belonging to the rhombic system.

B. H. B.

Beryl from Amelia Co., Virginia. By R. W. Baker (*Amer. Chem. J.*, **7**, 175—176).—The sample from Amelia Court House was transparent and of a rich honey-yellow colour; there were many microscopical fluid cavities. Analysis gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	BeO.	CaO.	Na_2O.	H_2O.
65·24	17·05	2·20	12·64	0·57	0·68	2·70 = 101·08.

The author holds that both water and alkalis are probably normal constituents of beryl. H. B.

Allanite from Nelson Co., Virginia. By C. Memminger (*Amer. Chem. J.*, **7**, 177—178).—The mineral occurs in rounded masses, covered with a thin yellowish-white coating. Lustre resinous; hardness 6; sp. gr. 3·59. Analysis gave:—

SiO_2.	SnO_2.	Al_2O_3.	Ce_2O_3.	Di_2O_3.	La_2O_3.	Fe_2O_3.	FeO.	CaO.
30·04	0·17	16·10	11·61	5·39	4·11	5·06	9·89	13·02

MgO.	Na_2O.	K_2O.	H_2O.
1·11	0·28	0·02	2·56 = 99·36

H. B.

A Decomposition Product of Allanite: a Variety of Kaolinite from Nelson Co., Virginia. By E. P. VALENTINE.—This brown, soft substance is produced by the weathering of the allanite described in the preceding Abstract. Analyses gave—

	SiO_2.	Al_2O_3.	Fe_2O_3.	Ce_2O_3.	La_2O_3.	Di_2O_3.	MgO.	K_2O.
I.	18·66	23·28	34·48	1·30	3·27	0·65	0·29	0·20
II.	21·37	20·66	12·24	21·90	—	—	—	—

	Na_2O.	BeO.	H_2O.	
I.	0·43	—	17·16 = 99·72	
II.	—	1·95	21·37 = 99·49	H. B.

Hornblende from St. Lawrence Co., New York. By G. H. WILLIAMS (*Jahrb. f. Min.*, 1885, **2**, Mem., 175—176).—The author has made a series of crystallographic observations on the green hornblende (pargasite) occurring at East Russel, St. Lawrence Co. The results are of interest on account of the discovery of two new planes: $\infty P\bar{5}$ and $\infty P\bar{7}$. The following forms were observed on several crystals: $\infty P\bar{\infty}$, $\infty P\bar{7}$, $\infty P\bar{5}$, $\infty P\bar{3}$, ∞P, $\infty P\bar{2}$, $\infty P\bar{3}$, $\infty P\bar{\infty}$.

B. H. B.

Amphibole-Anthophyllite from Baltimore. By G. H. WILLIAMS (*Jahrb. f. Min.*, 1885, **2**, Mem., 176—177).—The author describes an interesting occurrence of amphibole-anthophyllite, near Baltimore, which is perfectly similar to that described by Des Cloizeaux from Greenland and Norway. An analysis shows that the mineral is a typical anthophyllite; and from the optical examination there can be no doubt that it belongs to the monoclinic system. B. H. B.

Krokydolite and Arfvedsonite. By A. KENNGOTT (*Jahrb. f. Min.*, 1885, **2**, Mem., 163—167).—From a comparison of the published analyses of krokydolite and afvedsonite, the author concludes that krokydolite must be regarded as a fibrous variety of arfvedsonite. An analysis of the krokydolite associated with arfvedsonite in the zircon-syenite of Stavern in South Norway, would be of great value towards determining the relation between the two minerals.

B. H. B.

Alteration of Labradorite into an Albite and a Zeolitic Mineral. By KLOOS (*Jahrb. f. Min.*, 1885, **2**, Ref., 412—413).—In a rock from the Black Forest, consisting of plagioclase (labradorite), diallage, and hornblende, the author observed a gradual transition of the unaltered labradorite (Analysis 1) into a dull, milk-white, opaque mass, which was found under the microscope to consist of two minerals, a striated felspar and a finely granular mineral. The second mineral was soluble in dilute hydrochloric acid. II and III are analyses of the mixture, IV and V the plagioclase, and V the soluble, finely granular mineral.

	SiO_2.	Al_2O_3.	CaO.	MgO.	N_2O.	K_2O.	H_2O.
I.	51·53	31·41	13·00	--	3·49	0·57	—
II.	61·64	22·47	4·98	—	8·03	0·60	3·19
III.	58·02	24·00	7·45	0·25	6·43	0·44	3·11
IV.	64·87	21·54	2·28	—	8·78	1·33	—
V.	68·61	20·36	1·55	—	8·88	0·58	—
VI.	42·73	27·55	16·40	—	0·83	0·10	12·39

The newly formed plagioclase represents a mixture of 1 mol. anorthite and 8 mols. albite (IV), or 1 mol. anorthite and 10 mols. albite (V). The second mineral appears to be a zeolite with the molecular proportion of

$$Na_2O : CaO : Al_2O_3 : SiO_2 : H_2O = 1 : 21 : 19 : 51 : 49.$$

This constitution is approximately that of scolezite. B. H. B.

Alteration-pseudomorphs of Scapolite after Garnet. By A. Cathrein (*Jahrb. f. Min.*, 1885, **2**, 251).—Near the Castle of Achenrain, the author found an altered garnet contained in a fragment of amphibolite. The microscopic examination, the measurements of a pyramid 3P3, and the chemical analysis, indicate that the specimen is an alteration-product which resembles many scapolites, notably passauite. The analysis, it is true, was incomplete, as soda, potash, and chlorine were estimated by difference. The comparison of the analytical results with the theoretical composition of a mixture of 45 per cent. meionite silicate and 55 per cent. marialite silicate is fairly satisfactory, and the other observations clearly indicate that the white mineral surrounding the garnet-interior is scapolite. Epidote and labradorite appear as bye-products of the alteration.

B. H. B.

The Branchville Mica. By C. Rammelsberg (*Jahrb. f. Min.*, 1885, **2**, Mem., 225—228).—G. vom Rath presented the author with a large specimen of mica from Branchville, Connecticut. The specimen consists of grey, translucent mica (I), traversed in the middle by a broad layer of dark-brown mica (II). Analysis gave the following results:—

	F.	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	K_2O.	Na_2O.
I.	0·93	44·19	32·69	4·75	3·90	8·00	0·59
II.	2·43	40·14	23·43	7·65	11·87	9·64	1·13

	Li_2O.	H_2O.	Total.	Sp. gr.
I.	0·21	3·85	99·11	2·898
II.	1·18	2·64	100·11	3·030

Both micas appear to be new varieties of pure iron mica, their formulæ being—

I. $R'_{12}FeR_7Si_{11}O_{56}$.
II. $R'_8Fe_2R_4Si_9O_{36}$. B. H. B.

Chloritoïd containing Manganese. By E. Prost (*Jahrb. f. Min.*, 1885, **2**, Ref., 259).—This mineral, the salmite of Dumont,

occurs in the quartz veins which traverse the *phyllade salmien* of Vielsalm. It forms irregular masses with a finely granular texture, and greyish-green colour. H. = 5 to 6; sp. gr. 3·38. The mineral fuses with difficulty to a black enamel, and is imperfectly soluble in hydrochloric acid. The analysis gave the following results:—

Quartz.	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CoO.	MgO.
15·06	19·14	33·66	3·38	13·05	7·14	0·04	1·79

CaO.	H_2O.	Total.
0·30	6·32	99·88

This corresponds with the formula—

$$SiO_2,Al_2O_3,\tfrac{1}{3}MnO,\tfrac{2}{3}FeO,H_2O.$$

B. H. B.

Chlorite from Albemarle Co., Virginia. By M. Bird (*Amer. Chem. J.*, **7**, 181).—Olive-green, pearly scales; hardness 2·5; sp. gr. 3·05. Under the microscope, a small amount of hydrated ferric oxide is seen between the laminæ. Analysis gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	H_2O.	
23·52	22·35	1·92	28·78	0·32	0·39	10·79	11·28	= 99·35

H. B.

Some Ill-determined Minerals. By Heddle (*Min. Mag.*, **5**, 26—31; *Jahrb. f. Min.*, 1885, **2**, Ref., 260—262).—The following substances are described as ill-determined or doubtful species:—

Plynthite.—From Quiraing in Skye. It occurs in layers 1 to 2 inches thick in amygdaloid. Colour deep red, lustre greasy, sometimes earthy and dull. It falls to pieces in water, and may thus be distinguished from the accompanying massive mesolite. Its composition was found to be as follows:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	H_2O.	Total.
29·54	19·02	28·01	3·25	0·84	2·23	17·39	100·28

At 100° it loses 6·687 per cent. of moisture. At the Storr, in Skye, it occurs in a repeated series of beds. It is evidently merely bole.

Uigite.—The mineral, for which the name uigite is proposed, was found at Uig, 16 miles north of Portree, in Skye, with faröelite and analcime. It occurs indistinctly crystallised in small nests in the amygdaloid. In general appearance, it is intermediate between faröelite and gyrolite. Sp. gr. 2·284. Analyses gave the following results:—

	SiO_2.	Al_2O_3.	CaO.	Na_2O.	H_2O.	Total.
I.	46·32	21·35	16·36	4·69	12·21	100·93
II.	45·98	21·93	16·15	4·68	11·25	99·99

Uigite is thus either a mixture of faröelite and gyrolite, or a simple mineral.

Ferrite.—This mineral the author shows to be an alteration-product of either augite or olivine.

Craigtonite is the name given by the author to a substance occurring as a thin coating which adheres to red granite at Craigton, Aberdeenshire. Its colour is blue-black. The substance was dissolved off the granite by dilute hydrochloric acid, and gave on analysis the following results:—

Al_2O_3.	Fe_2O_3.	MnO.	MgO.	K_2O.	Na_2O.	Total.
32·20	38·30	7·46	16·61	4·74	0·68	99·99

Ellonite is the *ad interim* name given to a pale, dull, unctuous powder which occurs in small nests in gneiss at Ellon in Aberdeenshire. The associated minerals were orthoclase and lepidomelane. Analysis gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.
63·00	3·05	1·67	1·46	0·69	1·29	15·61

K_2O.	Na_2O.	H_2O.	Total.
0·63	0·79	11·70	99·89

At 100° it loses 6·365 per cent. of water. The powder may possibly be of the nature of cimolite or sepiolite. B. H. B.

Fibrous Bisilicate from Nelson Co., Virginia. By L. G. Patterson (*Amer. Chem. J.*, **7**, 180).—Wedge-shaped, fibrous, massive olive-green to dark-green layers, interpenetrating epidote rocks. Hardness 4; sp. gr. 3·153. Microscopically examined, it appears quite fresh. Analysis gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.
51·00	3·05	4·35	12·83	0·60	11·20	14·24	0·27

Na_2O.	H_2O.	
0·73	2·00	= 100·27

H. B.

Trachytes of the Eperies-Tokay Mountains. By S. Roth (*Jahrb. f. Min.*, 1885, **2**, Ref., 280—281).—The eruptive rocks of the northern portion of the Eperies-Tokay mountains are described partly as amphibole-trachytes, partly as augite-trachytes, and are divided into four geographical groups. The composition and structure of the amphibole-trachytes are normal; plagioclase (andesine and oligoclase), brown opaque or transparent, green crystals of hornblende, augite, magnetite, and apatite being constituents. Three analyses of amphibole-trachyte are given: I, from the Fintaer Straz; II, from the valley south of Krivi and Javor; III, from the road leading to Klauzura.

The augite-trachytes correspond in composition and structure with the normal augite-andesites. Two analyses are given: IV, from the Sosujfaluer mountain; V, from Dubnik. To this type belongs the mother-rock of the Dubnik opals.

	I.	II.	III.	IV.	V.
SiO_2	60·70	60·17	59·80	55·80	58·20
CaO	1·92	3·55	4·30	5·22	4·50
MgO	1·20	trace	trace	trace	trace
Fe_2O_3	9·20	10·20	7·10	10·80	8·60
Al_2O_3	19·70	17·40	18·30	20·00	21·40
K_2O	4·53	4·64	3·50	5·20	6·22
Na_2O	2·40	4·20	4·47	3·00	
P_2O_5	trace	trace	trace	trace	trace
H_2O	0·99	0·43	1·85	0·58	1·42
Totals	100·64	100·59	99·32	100·60	100·34

B. H. B.

Application of Thermochemistry to Geology: Zinc. By DIEULAFAIT (*Compt. rend.*, **101**, 842—845).—It is well known that the carbonate and sulphide are by far the most abundant naturally occurring compounds of zinc. Zinc carbonate is formed from the monoxide with development of heat, and no oxide higher than the monoxide is known; hence, when the zinc has been converted into carbonate it is in its state of most stable equilibrium, and the carbonate does not undergo oxidation like the corresponding compounds of iron and manganese.

Natural deposits of zinc carbonate are almost always associated with dolomitic rocks. Many metals, including zinc, which are now found in the form of carbonates, originally existed as sulphides. The zinc sulphide has been oxidised to the soluble sulphate, and this in course of time has been brought into contact with water holding in solution either calcium or magnesium carbonate, or both. Consideration of the following thermochemical data—

$ZnO + SO_3$ develops	11·7 cal.	$ZnO + CO_2$ develops	5·5 cal.
$CaO + CO_2$ „	9·8 „	$CaO + SO_3$ „	15·8 „
	21·5 „		21·3 „
$ZnO + SO_3$ develops	11·7 „	$ZnO + CO_2$ develops	5·5 „
$MgO + CO_2$ „	9·0 „	$MgO + SO_3$ „	15·6 „
	20·7 „		21·1 „

shows that with zinc sulphate and calcium carbonate the first system corresponds with the greatest development of heat, and hence will be formed in preference, or, in other words, the zinc will remain as sulphate; but in the case of zinc sulphate and magnesium carbonate the second system has the greatest heat of formation, and consequently the zinc sulphate will be converted into carbonate with simultaneous formation of magnesium sulphate. The salts of zinc are isomorphous with the corresponding salts of magnesium, and unite with them to form double compounds, hence when magnesium car-

bonate is deposited, any zinc carbonate existing in the same solution will also separate out. This conclusion agrees with the results of the author's previous researches on the formation of zinciferous dolomites in ancient seas.

The various natural forms of zinc carbonate may be grouped under three heads, namely, that associated with and disseminated throughout dolomitic rocks, which is the most abundant form; that existing in beds and strings contemporaneous with the rocks in which they are found; and that which is found in fissures and caverns in dolomitic rocks, and has been extracted from these rocks by some agency similar to that which has caused the formation of the deposits of calcium phosphate in the south-east of France.

Most probably all the zinc carbonate now found, originally existed in solution in water together with the constituents of dolomite, and it is therefore contemporaneous with the dolomitic rocks in which it occurs. The isolation of the zinc carbonate in masses is the result of subsequent secondary changes. C. H. B.

The Meteoric Iron of Santa Rosa, Colombia, 1810. By A. v. Lasaulx (*Jahrb. f. Min.*, 1885, **2**, Ref., 269—270).—The author has examined a fragment of the meteoric iron from Santa Rosa in Colombia, which Stübel himself broke off from the large block that lies in the market place of Santa Rosa. It is stated by Boussingault to have been found in 1810 at Tocavita. The block is, according to Stübel, 0·7 metre long, 0·6 broad, and 0·5 high, and weighs 75 kilos. The analysis gave 91·48 per cent. of iron and 8·20 per cent. of nickel, with some cobalt, 0·32 silicates, and traces of copper, carbon, phosphorus, and schreibersite. This analysis agrees with the analyses of the Rasgatà iron, so the meteorites of Santa Rosa and Rasgatà evidently fell at the same time. Olivine and colourless splinters of another silicate were observed, but the colourless grains, stated by Wöhler to occur in the Rasgatà iron, were absent. B. H. B.

The Bingera Meteorite. By A. Liversidge (*J. R. Soc. New South Wales*, **16**, 35—36; *Jahrb. f. Min.*, 1885, **2**, Ref., 271).—The meteorite, a meteoric iron, was found by some gold-miners at Bingera. It is pear-shaped, 2 inches long, and $1\frac{1}{2}$ inch thick at the thicker end, $\frac{1}{2}$ inch at the thinner. The total weight is 240·735 grams, the sp. gr. being 7·834 to 7·849. The surface is covered with a black, fused skin of magnetic oxide of iron. The skin is hard, brittle, and laminated. In places it is marked with sharply defined cracks, clearly the outlines of the Widmanstättian figures. The mass has well-marked polarity, the thin end being the south-seeking pole. On analysis, the following results were obtained:—

C.	Insol. in HCl.	Fe.	Ni.	Co.	P.	Total.
0·137	0·553	93·762	4·391	0·668	0·195	99·706

B. H. B.

Meteorites in the Public Collections of Mexico. By G. vom Rath (*Jahrb. f. Min.*, 1885, **2**, Ref., 270).—The following meteorites are described:—*From the National Museum:* an iron mass a

cubic foot in size from Xiquipilco, Toluca Valley, which has remained unaltered, whilst similar irons in Europe exfoliate; an iron meteorite of nearly the same size from the Hacienda Cacaria, 42 kilometres north of Durango; a meteorite, 421 lbs. in weight, from Yanhuitlan, Oaxaca, with 6·21 per cent. of nickel and 0·27 per cent. cobalt. *From the School of Mines:* a chondrite which fell 33 kilometres east of Dolores Hidalgo, Guanaxuato, and an iron meteorite from Santa Rosa, in the east of Coahuila. *From the Guanaxuato College:* a magnificent, crystalline-granular chondrite, 399 grams in weight, which fell on June 11, 1878, between 11 and 12 A.M., at La Charca, 8 kilometres from Irapuato. B. H. B.

The Deniliquin or Barratta Meteorite. By A. LIVERSIDGE (*J. R. Soc. New South Wales*, **16**, 31—34; *Jahrb. f. Min.*, 1885, **2**, Ref., 270—271).—A preliminary notice of this meteorite was published in 1872. It is a siderolite, and consists of various silicates and nickeliferous iron. Externally it is covered with a blackish, fused skin, the external portions to the depth of an inch being distinctly laminated. The structure is chondritic, most of the grains varying in size from $\frac{1}{16}$ to $\frac{1}{8}$ inch in diameter. Under the microscope they are seen to have an imperfectly crystalline structure. The meteorite is essentially a mixture of enstatite and a mineral resembling olivine, with small quantities of other silicates. The percentage of nickel-iron amounts to 3·93. The sp. gr. of the laminated crust is 3·382, and that of the interior 3·503; the sp. gr. of the whole mass, weighing 145 lbs., was found to be 3·387. After prolonged digestion in concentrated hydrochloric acid, 47·47 per cent. of the meteorite dissolved. The analysis gave the following results:—

SiO_2.	Cu.	Fe.	Fe_2O_3.	Al_2O_3.	Ni.	MnO.	CaO.	MgO.
40·28	0·18	14·96	3·93	1·84	4·22	0·73	1·40	23·73

K_2O.	Na_2O.	S.	P.	Cr, Co, C.	O.
1·02	0·99	2·29	0·61	traces	[3·78]

The analysis of the metallic portion, separated by means of a fine sieve, gave the following results:—

SiO_2.	Fe.	Ni.	Co.	P.	O.	S.
6·61	79·85	7·34	0·43	0·24	5·21	trace

A second portion from a different part of the meteorite gave—

Fe.	Ni + Co.	SiO_2.	Total.
91·25	7·20	1·55	100·00

Daubrée provisionally classes this meteorite with those of Tadjera, Orvinio, and Koursk. B. H. B.

Proportion of Bromine in Sea-water. By E. BERGLUND (*Ber.*, **18**, 2888—2890).—Former determinations of the relative proportion of bromine to chlorine in sea-water are very variable. By means of an improved method for the estimation of bromine in the

presence of chlorine, the author has made a series of determinations of milligrams of bromine to 100 grams of chlorine, and of the proportion of chlorine in grams per litre in sea-water from various sources. The mean results are approximately equal to those obtained by Dittmar (Report of Voyage of "Challenger"), namely, 340 mgrms. of bromine to 100 grams chlorine, and 19·5 grams chlorine per litre. V. H. V.

Organic Chemistry.

Volatility of Mixed Derivatives. By L. Henry (*Compt. rend.*, **101**, 816—818).—The boiling points of mixed derivatives of the type = CXX′, which contain equivalent radicles X and X′ *of analogous functions* are the means of the boiling points of the corresponding simple derivatives, CX_2 and CX'_2. The following table contains examples selected from the large number given by the author.

	B. p.		B. p.
CH_2Cl_2.....	41·0°	CH_2Br_2.....	98·0°
$CHCl_3$	61·2	$CHClBr_2$	123—125°
$CO(OMe)_2$.....	91·0	$CO(OEt)_2$.....	126°
$CH_3{\cdot}CHCl_2$....	60·0	$CH_3{\cdot}CHBr_2$	110
$CH_3{\cdot}CH(OMe)_2$	64·0	$CH_3{\cdot}CH(OEt)_2$..	104
$CH_2Br{\cdot}CHCl_2$ ..	137—138°	$CH_2Br{\cdot}CHBr_2$...	186—187°

	B. p.
CH_2ClBr	68—69°
$CHCl_2Br$	91—92
$OMe{\cdot}COOEt$	109°
$CH_3{\cdot}CHClBr$	84—85°
$OEt{\cdot}CHMe{\cdot}OMe$	85°
$CH_2Br{\cdot}CHClBr$	162—163°

The law holds good whether substitution has taken place in the CH_3 or CH group or in both together.

If, however, the radicles, although equivalent, have different functions, the boiling point of the mixed derivatives is sensibly higher than the mean of the boiling points of the corresponding simple derivatives.

	B. p.		B. p.
CH_2Cl_2.....	40—41°	$CH_2(OMe)_2$	42°
$COCl_2$	8°	$CO(OEt)_2$	126
$CH_3{\cdot}CHCl_2$....	60	$CH_3{\cdot}CH(AcO)_2$.	169

	B. p.
$CH\,Cl{\cdot}OMe$	59°
$COCl{\cdot}OEt$	94
$CH_3{\cdot}CHCl{\cdot}AcO$.....	125

Analogous relations are observed in the case of mixed polycarbon derivatives, XC . . . CX′ in which the two radicles are combined with different atoms of carbon. C. H. B.

Formation of Propylene from Glycerol. By A. Claus (*Ber.*, **18**, 2931; compare Abstr., 1882, 1038).—The yield of propylene is satisfactory only when a large amount of glycerol (1 kilo.) is distilled as quickly as possible with twice its weight of zinc-dust. Westphal has shown (*Inaug. Diss.*, Freiburg, 1877), that acraldehyde, allyl alcohol, and two condensation products, $C_6H_{10}O$ and $C_{12}H_{20}O_2$, boiling at 140° and 200° respectively, are formed in the reaction. Both condensation compounds when oxidised yield propionic acid and carbonic anhydride. N. H. M.

Action of Chlorine on Trimethylethylene. By N. Kondakoff (*J. Russ. Chem. Soc.*, 1885, 290—319).—Trimethylethylene may be prepared either by the action of dilute sulphuric acid on tertiary amyl alcohol, or by treating tertiary amyl iodide with alcoholic potash; as the amylene obtained by the first method contains as a rule an admixture of asymmetrical methylethylethylene, the author used the latter method in most of his experiments. Tertiary amyl iodide distils almost entirely at 124—125°, not at 127—129° as stated by other investigators. The amylene obtained from this iodide was converted into bromide, and the latter heated with lead oxide and water in a sealed tube: methyl isopropyl ketone was formed and not an aldehyde, as would have been the case were methylethylethylene present (Eltekoff, Abstr., 1883, 566). When a current of chlorine gas is passed into trimethylethylene (the temperature being either − 20° or + 20°, or finally + 38°, the boiling point of the hydrocarbon), it was observed that up to a certain point only absorption of the gas takes place, but in a short time this ceases, and hydrogen chloride is evolved until the end of the operation. The products of the reaction differ slightly according to the temperature. In the cold, high boiling products (160—180°) are formed along with more volatile compounds; at the ordinary temperature, the whole of the product distils below 135°; the compounds obtained at 38° all pass over below 110°. The chlorinated product more especially investigated was obtained at the ordinary temperature. Seven fractions were obtained on distillation: the first consisted chiefly of unchanged trimethylethylene, the last did not contain any unsaturated compounds. The intermediate fractions strongly decolorise bromine and contain No. 3 (the main portion boiling between 90—95°), 64, No. 4, 67, and No. 5, 60 per cent. of C_5H_9Cl. When treated with water, the fractions 2, 3, and 4 were entirely dissolved, 5 and 6 dissolved partly, leaving an oil free from unsaturated compounds. The aqueous solution contains, in addition to tertiary amyl alcohol, an unsaturated alcohol, $C_5H_{10}O$, boiling at 115—117°; sp. gr. at 0° = 0·8571 and at 20·5° = 0·8419. This unites readily with bromine, reacts with phosphorus pentachloride, and yields a crystalline sodium-derivative. The bromide and acetate were prepared, the latter boiling at 130—131°. The data for the etherification of the alcohol, proved it to be a secondary

alcohol. By the action of dilute acids at 100° it is transformed into methyl isopropyl ketone. It is therefore methyl isopropenyl carbinol, $CH_2 : CMe \cdot CHMe \cdot OH$, the chlorinated compound obtained from trimethylethylene having an analogous structure. The fraction of the chlorine-derivatives boiling at 133—135° contains the chloride $C_5H_{10}Cl_2$, a heavy oil, which is also left when the portions 5 and 6 of the distillate are treated with water. A. T.

Fulminic Acid. By L. Scholvien (*J. pr. Chem.* [2], **32**, 461—489).—A continuation of Carstanjen and Ehrenberg's work on the fulminates (Abstr., 1882, 816). When dilute sulphuric acid (1 : 5) acts on sodium fulminate and the mixture is kept well cooled, a yellow liquid is obtained, which on treatment with ether yields an ethereal solution of fulminic acid. This solution is very unstable, and the fulminic acid is rapidly converted into two isomeric acids, isocyanuric acid and isocyanilic acid. The presence of free fulminic acid in the ethereal solution was proved by separating it very rapidly from the mother-liquor, and shaking it with an aqueous silver solution, when a white precipitate of silver fulminate separated immediately; if the ethereal solution was allowed to remain for ten minutes and then shaken with the silver solution, red silver isocyanurate separated and isocyanilic acid remained in solution.

Isocyanuric acid gives coloured salts containing one, two, and three equivalents of metal; when evaporated with hydrochloric acid it yields hydroxylamine; with potash, ammonia is given off. The pure acid, $C_3N_3O_3H_3 + 3H_2O$, forms a white, crystalline powder, melting at 81°, and exploding with great violence at 106°. When kept for a long time it is converted into an isomeric acid, *β-isofulminuric acid;* this crystallises in small needles of vitreous lustre, when anhydrous melts at 196° with decomposition, and is not acted on by hydrochloric acid.

Isocyanilic acid, HCNO, crystallises in white lustrous needles; when heated it decomposes without previous fusion; it forms unstable salts, and is not acted on by hydrochloric acid. Boiled with potash it yields an acid, isomeric with Städeler and Strecker's "Uroxanic acid"; this forms a dark violet potassium salt.

When thiocarbamide is acted on by mercury fulminate, a mixture of thiocarbamide, mercury thiocyanate, carbonic anhydride, mercury sulphide and carbamide is formed. G. H. M.

Decomposition of Butylene and Amylene Hydrate by Heat. By Wolkoff and Bougaieff (*J. Russ. Chem. Soc.*, 1885, 276).—Butylene hydrate (secondary butyl alcohol) when heated in sealed tubes at 240—250° for 8—16 hours is not decomposed, but if the least quantity of a hydracid (hydriodic acid or even methyl iodide) be added, decomposition takes place at 220°, and pseudobutylene is formed after the lapse of only five to six hours. Similar observations were made with dimethyl ethyl carbinol and methyl isopropyl carbinol and some other alcohols; tertiary alcohols suffer this decomposition

most easily, primary alcohol with much more difficulty; normal alcohols have not yet been studied in this direction. A. T.

Preparation of Hexyl Glycerol. By P. Orloff (*J. Russ. Chem. Soc.*, 1885, Abstr., 146).—Hexylglycerol previously obtained by the author from dibromhydrin is best prepared by the action of diluted aqueous potash on the monochlorhydrin, the latter being formed by addition of hypochlorous acid to dimethyl allyl carbinol. The iodhydrin is obtained by the action of mercuric oxide and iodine on dimethyl allyl carbinol in the presence of water. The glycerol itself, when treated with fuming hydriodic acid and phosphorus, yields, besides a small amount of a crystalline compound not yet examined, an iodide distilling at 140—150°, and converted by alcoholic potash into a hexylene identical with Jawein's (Abstr., 1878, 961). A. T.

Decomposition of Galactose and Arabinose by Dilute Acids. By M. Conrad and M. Guthzeit (*Ber.*, **18**, 2905—2907).—The following results were obtained by heating 10·5 grams of galactose, 50 grams of water, and 4·87—4·84 grams of hydrochloric acid for 17 hours:—

Humic substances.	Unaltered galactose.	Acetopropionic acid.	Formic acid.
1·60	3·60	2·84	1·05
1·77	3·05	2·85	1·10

On replacing hydrochloric by sulphuric acid of the same concentration, the quantity of the decomposition product obtained was considerably less.

A specimen of arabinose from marc of beet-sugar melted at 158—160°; its specific rotatory power for a 10 per cent. solution was found to be $[\alpha]_D = 104°$; on heating 10·5 grams with hydrochloric acid under the same conditions as above, there were obtained 4·3 grams of humic substances, 0·42 gram of formic, and 1·24 gram of acetopropionic acid. These results tend to show that galactose and arabinose are not identical. V. H. V.

Raffinose or Melitose from Molasses, Cotton-seeds, and Eucalyptus Manna. By P. Rischbiet and B. Tollens (*Ber.*, **18**, 2611—2616).—From a consideration of the properties and reactions of this substance, and especially from the composition of the sodium-derivative and the amount of mucic acid formed on oxidation, the authors conclude that it is best represented by the formula $C_{36}H_{64}O_{32} + 10H_2O$. When boiled for some time with acids, a sugar crystallising in six-sided tables (probably galactose) is obtained. A comparison of melitose, from the manna of *Eucalyptus viminalis*, with raffinose shows the two substances to be identical; the name melitose is therefore preferable. A. J. G.

Action of Oxymethylene on Amines. By S. Kolotoff (*J. Russ. Chem. Soc.*, 1885, 229—251). — It is known that oxymethylene reacting with ammonia forms hexamethylenamine; the author has

studied the reaction with mono-, di-, and tri-ethylamine and aniline. *Ethylmethylenamine*, C_3H_7N, obtained from oxymethylene and ethylamine, is a colourless, alkaline liquid, boiling at 205—208°. The vapour-density determination and the analysis of the platinochloride show that the molecule of the compound is not polymeric, one molecule of each of the constituents entering into reaction. A solution of the base in hydrochloric acid, on remaining in a vacuum, is decomposed into ethylamine and oxymethylene. With diethylamine, a similar compound, $CH_2N_2Et_4$, was obtained as a bright colourless liquid boiling at 166—169°, and having a well-defined basic character. Triethylamine, as was expected, does not react with oxymethylene; thus in the reaction of oxymethylene with amines, the oxygen of the former combines with all the amidic hydrogen of the amine-group, forming water, whilst the two remaining radicles, uniting, form basic compounds. Aniline reacts very readily with oxymethylene, the mixture at once solidifying to a basic compound, which melts at 137—138° with decomposition, and forms a solid substance which does not melt even at 200°, the temperature of its decomposition. Heated with water at 100°, phenylmethylenamine splits up into aniline and oxymethylene. According to the author the molecule of the compound corresponds not with the simplest, but with a higher, probably doubled, formula. A. T.

Imines. By A. Ladenburg (*Ber.*, **18**, 2956—2961; comp. Abstr., 1883, 910).—Pentamethylenediamine is prepared by adding sodium as quickly as possible to a solution of trimethylene cyanide in boiling alcohol; the product is poured into water, and the alcohol distilled off. A trace of ammonia is evolved, and a small quantity of piperidine goes over with the alcohol. The pentamethylenediamine is then distilled with superheated steam, the distillate treated with a slight excess of dilute hydrochloric acid, and evaporated to dryness. The free base is obtained by dissolving the residue in a little water, adding potash and extracting with ether. The yield of base is 80 per cent. of the weight of cyanide employed. It is a colourless, syrupy liquid boiling at 175—178°. When exposed to air, it fumes and absorbs water and carbonic anhydride. It dissolves sparingly in ether, readily in alcohol and water. The *acetyl-derivative*, $C_5H_{10}(NHAc)_2$, is a crystalline substance; it boils above 360°. The formation of piperidine in the reaction is fresh evidence in support of the formula ascribed to it, and also explains its relation to tri- and penta-methylene-compounds: piperidine is *pentamethylenimine*. The author thinks it probable that all cyanides may be converted into amido-compounds by the method above described. N. H. M.

Bicuhyba Fat. By H. Noerdlinger (*Ber.*, **18**, 2617—2623).—Bicuhyba nuts, from *Myristica officinalis* or *M. bicuhyba*, give the following results on proximate analysis:—

Water	8·86
Ash	4·50
Fat	17·74
Crude fibre	30·62
Proteïds	17·62
Non-nitrogenous extractives	20·66

The results of the examination of the fat are very similar to those obtained by Reimer and Will (Abstr., 1885, 1197) with the fat of the fruit of *M. Surinamensis*; it consists mainly of trimyristin and triolein with small quantities of resin and free myristic acid, and very slight amounts of ethereal oils, volatile acids, and of a non-saponifiable oil. A. J. G.

β-Dimethacrylic Acid. By D. Oustinoff (*J. Russ. Chem. Soc.*, 1885, 439—448). — β-Diethylenelactic acid, obtained by oxidising allyl dimethyl carbinol, was distilled with dilute sulphuric acid (comp. Schirokoff, Abstr., 1880, 382). The dimethacrylic acid formed was purified by converting it into the zinc salt, decomposing this and crystallising the acid from water; it melts at 69·5—70°. The sodium, calcium, barium, zinc, copper, lead, and silver salts were examined as well as the dibromide, melting at 105—106° and resolidifying at 76°. The author gives a comparative table of the principal salts and dibromides of dimethacrylic acid, $CMe_2 : CH\cdot COOH$, and of its isomerides, angelic, methylcrotonic, and allylacetic acids.

A. T.

Oxidation of Oleic and Elaidic Acids with Potassium Permanganate in Alkaline Solution. By A. Saytzeff (*J. Russ. Chem. Soc.*, 1885, 417—435).—Oleic acid when treated with potassium permanganate in the presence of an excess of potash, yields *dihydroxystearic acid*, $C_{17}H_{33}(OH)_2\cdot COOH$, a crystalline acid insoluble in water, easily soluble in boiling, but sparingly in cold alcohol, and in hot ether. It melts after repeated purification at 136·5°, and solidifies again at 122—119°. When heated in a sealed tube at 120—130° with hydriodic acid, or by the action of phosphorus tri-iodide and water, it is converted into liquid iodostearic acid, the latter by reduction with zinc and hydrochloric acid yielding ordinary stearic acid. Iodostearic acid and silver oxide give hydroxystearic acid, melting at 83·5—85·5°, and solidifying at 68—63°. The dihydroxy-acid is identical with the isodihydroxystearic acid of Overbeck (*Annalen*, **140**, 72); the description of the properties of the acid given by Overbeck is inaccurate.

Dihydroxystearic acid, when distilled under a pressure of 100—150 mm., yields a crystalline acid, melting at 77—79°, and resolidifying at 69—66°; the analytical results approximate to the formula $C_{18}H_{34}O_3$; it would, therefore, seem to be formed by elimination of 1 mol. H_2O from dihydroxystearic acid.

The oxidation of elaidic acid under the above conditions yields an acid of the same composition as dihydroxystearic acid, but entirely differing from it in its properties; it melts at 99—100°, resolidifies at

86—85°, and is much more soluble in ether and in alcohol. The small amount of material did not admit of further study.

Oleic acid when treated with potassium permanganate alone seems to yield azelaic acid, although this could not be obtained in a state of purity from the products of the reaction. A. T.

Lactic Acid from Levulose. By V. Sorokine (*J. Russ. Chem. Soc.*, 1885, 368—369).—Amongst the products of the action of bases (caustic soda and baryta) upon levulose, the author finds lactic acid; it seems, therefore, that the formation of lactic acid from glucose by the action of bases is a reaction characteristic of all the substances of this group, similarly to the formation of levulinic acid under the influence of acids. Experiments are being made in order to determine the quantity of lactic acid formed in this reaction under varied conditions. A. T.

Action of Ammonia on Succinimide. By Roubtzoff (*J. Russ. Chem. Soc.*, 1885, 277—278).—When ammonia is passed over powdered succinimide placed in glass tubes and cooled to — 10° or — 20°, the tubes being then sealed and heated to 100—200°, succinamide is formed. At the ordinary temperature ammonia is not taken up, and the amide is not formed. A. T.

Ethyl Diacetofumarate. By F. Just (*Ber.*, **18**, 2636—2637).—By the action of sodium ethoxide on a solution of ethyl diacetosuccinate and precipitation with ether, the compound

$$COOEt{\cdot}CNaAc{\cdot}CNaAc{\cdot}COOEt$$

is obtained as a white powder. This when treated with an ethereal solution of iodine yields *ethyl diacetofumarate*,

$$COOEt{\cdot}CAc : CAc{\cdot}COOEt,$$

as a colourless oil which solidifies to long, silky needles, melting at 95·5—96°. Its reaction with phenylhydrazine is being studied.

A. J. G.

Non-volatile Product of the Oxidation of the Hydrocarbon $C_{12}H_{20}$. By A. Albitzky and V. Nikolsky (*J. Russ. Chem. Soc.*, 1885, 435—439).—Amongst the products of the oxidation with chromic mixtures, of the hydrocarbon $C_{12}H_{20}$ from allyl dimethyl carbinol, a syrupy acid, not volatilising with steam, has been obtained (Abstr., 1883, 1074). The authors have made analyses of its barium, calcium, and ethyl salts; although the results best agree with the formula $C_{10}H_{16}O_6$, it is more probably $C_{10}H_{18}O_6$, the latter formula being more in accordance with the structure of the hydrocarbon $C_{12}H_{20}$.

A. T.

Action of Ammonia on Parabanic Acid. By Miss Roudinskaia (*J. Russ. Chem. Soc.*, 1885, 278—279).—Ammonium parabanate when heated in a sealed tube at above 160°, is to a large extent converted into oxaluramide; at 100° the salt is decomposed, but scarcely any amide is formed. The same amide is obtained by passing

ammonia over parabanic acid at 130°; at lower temperatures ammonium parabanate is formed. From a few experiments, it appears that the formation of oxaluramide from ammonium parabanate (probably consisting in a decomposition of the salt into ammonia and parabanic acid, and subsequent formation of amide) is not only influenced by temperature, but also by the pressure of the gaseous product of the decomposition. A. T.

Aromatic Hydrocarbons in Caucasian Petroleum. By S. Doroshenko (*J. Russ. Chem. Soc.*, 1885, 285—290).—The presence of aromatic hydrocarbons in Caucasian petroleum has been shown by Markownikoff and Oglobline (Abstr., 1883, 564), who found hydrocarbons belonging to the higher isologous series in fractions of petroleum boiling between 150—210° and above 270°. It is, therefore, highly probable that the lower homologues of the benzene series might be present in the portions of petroleum hydrocarbons boiling below 150°. The material for the present investigation consisted (1) of portions of Bibi-Aïbat petroleum boiling at 105—115° and 115—125°, and (2) of a mixture of the products of purification of Balakhani petroleum boiling below 100°, and of Bibi-Aïbat oil boiling at 100—120°. The hydrocarbons were converted into sulphonic acids by treatment with sulphuric acid, and these distilled with calcium hydroxide. The amount of oil thus obtained did not exceed 10 per cent. of the sulphonic acids; the hydrocarbons were subjected to fractional distillation, and fractions boiling at 75—95°, 95—110°, 110—120°, 120—130°, 130—135, 135—141° were collected. In the first portion benzene was shown to be present by its separation in crystals on cooling the oil to − 30°; in the higher boiling distillates, the presence of toluene also was shown. The portion boiling at 75—110° was nitrated in the cold, and the nitro-products, which had a decided smell of nitrobenzene, reduced with tin and hydrochloric acid, when aniline and toluidine were formed. Toluene is also contained in the fraction 110—120°. The portions boiling between 130° and 141° contain isoxylene. During the dry distillation of the sulphonic acids with calcium hydroxide, a crystalline substance melting at 192·5—194°, was deposited in the condenser, and was also obtained on cooling the hydrocarbons boiling above 140°. Its quantity was too small for analysis, and the author only points out its resemblance to methylenediphenylene obtained by Carnelley on passing a mixture of toluene and benzene vapours through a red-hot tube (Trans., 1880, 710). A. T.

Oxidation of Benzene-derivatives with Potassium Ferricyanide. By W. A. Noyes (*Amer. Chem. J.*, **7**, 145—149; comp. Abstr., 1884, 299).—Orthobromotoluene when oxidised with an alkaline ferricyanide, yields orthobromobenzoic acid, but oxidation occurs only to a very slight extent, less than 0·5 per cent. being formed during three or four hours.

Paratoluenesulphonamide yields 55 per cent. of the corresponding parasulphaminebenzoic acid; the barium salt, $(C_7H_6SO_4N)_2Ba + 5H_2O$, separates in crystalline tufts from a cold solution, whilst from

a hot solution it separates with $2H_2O$ in small scales; this salt has been described by Remsen as crystallising with only 1 mol. H_2O.

H. B.

Oxidation of Metanitrotoluene. By W. A. Noyes and W. E. Moses (*Amer. Chem. J.*, **7**, 149—153; comp. Abstr., 1884, 299).—When metanitrotoluene is oxidised with alkaline ferricyanide, not more than 5 per cent. of metanitrobenzoic acid was obtained, whilst the para- and ortho-nitrotoluenes yield 70 to 75 per cent. of the corresponding acids; it would, therefore, seem probable that an alkaline ferricyanide solution can be used to oxidise a methyl-group standing in the ortho-position to a nitro-group without attacking a methyl-group in the meta-position. H. B.

Ortho-xylenyl Chloride. By E. Hjelt (*Ber.*, **18**, 2879—2881).—If chlorine is passed into ortho-xylene until the gain in weight corresponds with the replacement of 4 atoms of hydrogen by chlorine, a crystalline mass saturated with an oil is produced. On distillation, a liquid and a crystalline solid are obtained; the latter is a *tetrachloride*. It melts at 89° and boils at 273—274°, is insoluble in water, readily soluble in ether; it crystallises in the triclinic system with axial ratio $a : b : c = 0{\cdot}972 : 1 : 0{\cdot}741$. In order to determine whether the chlorine-atoms are disposed symmetrically or unsymmetrically, the compound was heated with water in a sealed tube at 200—210°: phthalide was obtained in large quantities, a result which would point to the latter hypothesis; but inasmuch as the phthalide was always accompanied, especially at the lower temperature, by an oil having aldehydic properties, the author is inclined to regard the substance as having the formula $C_6H_4(CHCl_2)_2$.

V. H. V.

Reaction of Aluminium Chloride with Hydroxyl Compounds. By A. Claus and H. Mercklin (*Ber.*, **18**, 2932—2936).—*Dichlorhydrin-aluminium chloride*, $Al_2Cl_4(O{\cdot}C_3H_5Cl_2)_2$, is obtained by the action of aluminium chloride on dichlorhydrin dissolved in carbon bisulphide. It is a crystalline, hygroscopic substance.

Triphenol-aluminium chloride, $Al_2Cl_3(OPh)_3$, is prepared by adding aluminium chloride in small quantities to a solution of phenol in boiling carbon bisulphide; it forms a yellow powder readily soluble in boiling carbon bisulphide.

Resorcinol-aluminium chloride, $Al_2Cl_4 : C_6H_4O_2$, forms a thick reddish-brown liquid, which gradually becomes solid when kept over sulphuric acid; it dissolves readily in hot carbon bisulphide. All these compounds decompose violently when brought into contact with water.

Symmetrical triphenylpropane, $C_3H_5Ph_3$, is prepared from trichlor- or tribrom-hydrin and forms a thick, yellow liquid which distils without decomposition only under diminished pressure. Diphenylpropane is formed at the same time. N. H. M.

Pseudocumenol and Pseudocumidine. By K. Auwers (*Ber.*, **18**, 2655—2663).—By the action of bromoform and aqueous alkalis on pseudocumenol, a compound, $C_{10}H_{12}Br_2O$, is obtained, which melts

at 105°, and resembles the chlorine compound described in the author's previous communication (Abstr., 1885, 380) in all respects save in its ready decomposition by alcoholic potash, by which the chlorine compound is not affected at 100°. By the action of iodoform on pseudocumenol, only a very small quantity of an iodo-compound is formed. Similar products cannot be obtained from phenol, triphenyl orthoformate being formed.

Dibromopseudocumenyl methyl ether, $C_6Br_2Me_3{\cdot}OMe$[2 : 5 : 1 : 3 : 4 : 6], is obtained by brominating pseudocumenyl methyl ether at the ordinary temperature, or by methylating dibromopseudocumenol. It crystallises in white needles of vitreous lustre, melts at 96°, is insoluble in water, readily soluble in alcohol and acetic acid, very readily soluble in ether, chloroform, and benzene, and is only slightly attacked when heated with hydrochloric acid at 170°.

Metanitropseudocumenol, $OH{\cdot}C_6HMe_3{\cdot}NO_2$ [$Me_3 : NO_2 : OH$ = 1 : 3 : 4 : 2 : 6], is prepared by evaporating an alcoholic solution of its nitrate (*loc. cit.*) to a syrup and then distilling with steam, and is also obtained by adding concentrated hydrochloric acid to an alcoholic solution of the nitrate, and allowing the mixture to remain for some time. It crystallises in long, reddish-yellow needles or prisms of fatty lustre, melts at 48°, and is moderately soluble in hot water, readily in the other usual solvents. The nitrate of this substance is also formed when pseudocumenyl methyl ether is nitrated. *Metanitropseudocumenyl methyl ether*, $NO_2{\cdot}C_6HMe_3{\cdot}OMe$, is prepared by methylating metanitrocumenol; it crystallises in large prisms and rhombic tables, melts at 41—42°, and is very readily soluble in the ordinary solvents except water. The following corrections are made in the melting points previously given (*loc. cit.*): dinitropseudocumenol melts at 112°, dipseudocumenol at 173°, and dipseudocumenyl methyl ether at 126°.

Dibromodipseudocumenol, $C_{18}H_{20}Br_2O_2$, crystallises in small, lustrous crystals, and melts at 186—187°.

Dipseudocumidine, when pure, melts at 68° and boils at 234°; acetopseudocumide melts at 164° and boils at above 360°; orthonitracetopseudocumide melts at 202—204°. *Dinitracetopseudocumide*,

$$C_6Me_3(NO_2)_2{\cdot}NHAc\ [1 : 3 : 4 : 2 : 5 : 6],$$

melts at 280°, sublimes unchanged, and is insoluble in water, and sparingly soluble in other solvents. If this is heated with concentrated sulphuric acid for a few minutes at 100°, and a large quantity of water is then added, *dinitropseudocumidine*, $C_6Me_3(NO_2)_2{\cdot}NH_2$, is precipitated. This crystallises in long, lustrous, orange-yellow needles, melts at 183°, and has but very feeble basic properties. When reduced with tin and hydrochloric acid, it yields the hydrochloride of a base whose composition could not be ascertained with certainty. The hydrochloride crystallises in plates or prisms, the free base forms silky needles.

Amidopseudocumylenethenylamidine, $NH_2{\cdot}C_6Me_3{<}\overset{\text{--N}}{\underset{\text{NH}}{}}{>}CMe$, is prepared by reducing dinitracetopseudocumide with tin and hydrochloric acid. It crystallises with 2 mols. H_2O in pale-yellow prisms or stellate

groups of plates, softens at 215°, and melts at 215—218°. The hydrochloride, $C_{11}H_{15}N_3,2HCl + Aq$, crystallises in slender, white needles; a monohydrochloride, $C_{11}H_{15}N_3,HCl + 2H_2O$, crystallises in slender, white prisms; the platinochloride, $C_{11}H_{15}N_3,H_2PtCl_6$, forms stellate groups of slender, orange-red prisms. A. J. G.

Action of Acetone on Aniline. By C. Beyer (*J. pr. Chem.* [2], **30**, 489—491).—An answer to Engler and Riehm regarding priority.

Remarks on the Preceding "Answer." By E. v. Meyer (*J. pr. Chem.* [2], **30**, 491).

Consecutive Xylidines. By E. Wroblewski (*Ber.*, **18**, 2904—2905).—A controversial paper.

Commercial Xylidine. By W. Staedel and O. Hölz (*Ber.*, **18**, 2919—2924).—Commercial xylidine consists of two isomeric modifications: the one a metaxylidine [Me : Me : NH_2 = 1 : 3 : 4]; the other a paraxylidine. The former boils at 212°, and its acetyl-derivative at 130°; its corresponding xylenol is not, as Jacobsen described, a liquid, but a solid crystallising in needles which melt at 28°, sparingly soluble in water, the aqueous solution giving a blue coloration with ferric chloride.

On oxidation with chromic acid, the paraxylidine yields a quinone. The corresponding quinol forms a dibenzoyl-derivative, $C_6H_2Me_2(OBz)_2$, crystallising in glistening needles which melt at 160°. The diethyl-derivative, $C_6H_2Me(OEt)_2$, forms glistening white leaflets melting at 106°. V. H. V.

Simple Method of Preparing Azo-derivatives. By O. N. Witt (*Ber.*, **18**, 2912—2913).—After alluding to the various difficulties incidental to the methods of preparation hitherto proposed for the azo-derivatives, the following simple process is suggested. A quantity of stannous chloride equivalent to that of the nitro-compound, is poured into an excess of soda, and the solution formed is heated with the nitro-compound at the temperature of the water-bath. The process is suitably modified according to the nature and stability of the compound which it is required to reduce. Usually the azo-salt crystallises out on cooling, but if this does not occur, then the stannous oxide is precipitated by a current of carbonic anhydride, the liquid filtered and evaporated, and the azo-derivative finally separated from the potassium carbonate by aqueous alcohol. V. H. V.

Azo-compounds with Mixed and Substituted Radicles and their Derivatives. By T. Kanonnikoff (*J. Russ. Chem. Soc.*, 1885, 369—371).—In manner similar to the formation of hydroxyazobenzene from diazobenzene and phenol, new azo-compounds were obtained from orthoanisidine and metacresol, from orthoanisidine and orthocresol, and from orthonitranisoïl by reducing them with sodium amalgam. The first, $OMe\cdot C_6H_4\cdot N_2\cdot C_6H_3Me\cdot OH$, melts at 161°, the second at 68°, and the third at 103°. The reduction of these isomeric

compounds with stannous chloride and hydrochloric acid yields substances corresponding with benzidine and diphenylene. The chief aim of further investigation will be the study of Skraup's reaction with the compounds containing amido-groups. Thus far, on heating meta-cresolorthoanisoïl and azorthoanisoïl with glycerol-sulphuric acid and nitrophenol, compounds of basic character are obtained which form well crystallised salts. A. T.

Derivatives of Dicyanphenylhydrazine. By J. A. Bladin (*Ber.*, **18**, 2907—2912).—By the action of nitrous acid on dicyanphenylhydrazine, a compound, $C_8H_5N_5$, is obtained (Abstr., 1885, 980) to which the formula $N\lessdot^{N\cdot N}_{NPh}\gtrdot C\cdot CN$ is now ascribed. This, when saponified, yields the corresponding *carboxylic acid*,

$$N\lessdot^{N\cdot N}_{NPh}\gtrdot C\cdot COOH,$$

crystallising with 1 mol. H_2O in colourless needles; when dried it melts at 137—138°, and is decomposed with evolution of carbonic anhydride at 150°. Its *potassium* salt forms glistening leaflets, *copper* salt, bluish-green rhombic tables, *silver* and *lead* salts, sparingly soluble crystalline precipitates. The *methyl* salt, $CN_4Ph\cdot COOMe$, crystallises in glistening leaflets melting at 116°, soluble in alcohol and ether, sparingly soluble in water; the *ethyl* salt forms colourless needles melting at 74°.

Hydrogen peroxide converts the nitrile, $PhCN_4\cdot CN$, into the corresponding *amide*, $CN_4Ph\cdot CONH_2$, which crystallises in colourless prisms melting at 168°, sparingly soluble in water, alcohol, and ether.

On heating the carboxylic acid, an oil is obtained of the composition $C_7N_6N_4 = N\lessdot^{N\cdot N}_{NPh}\gtrdot CH$; it is heavier than and insoluble in water, readily soluble in alcohol and ether, is readily decomposed on distillation, and has feebly basic properties, dissolving in concentrated acids, and yielding a *platinochloride* in the form of golden leaflets.

V. H. V.

Indophenol and Indoaniline. By R. Möhlau (*Ber.*, **18**, 2913—2918).—The researches of Caro, Nietski and others, have shown that the simultaneous oxidation of paradiamines or amidophenols on the one hand, and of phenols and amines on the other, yields a number of dyes belonging to the safranine, or indophenol and indoaniline groups. In this paper phenol- and α-naphthol-blues and their derivatives are more particularly studied.

Phenol-blue, $C_{14}H_{14}N_2O$, is best prepared by heating the double chloride of zinc and dimethylphenylene-green with soda solution (sp. gr. = 1·4); a flocculent blue precipitate separates out, which on boiling with a 10 per cent. grape-sugar solution, evolves dimethylamine and dissolves to form a red liquid. On filtration and exposure of the liquid to the air, the phenol-blue separates out in glistening, prismatic crystals. The reaction is explained thus:—

$$C_6H_4\begin{cases}N{\cdot}C_6H_4{\cdot}NMe_2\\ |\\ NMe_2Cl\end{cases} + NaOH = NaCl + C_6H_4\begin{cases}N{\cdot}C_6H_4{\cdot}NMe_2\\ |\\ NMe_2{\cdot}OH\end{cases}$$

$$= <^{C_6H_4}_{-O-}>N{\cdot}C_6H_4{\cdot}NMe_2 + NHMe_2.$$

In the above operation, if a larger proportion of soda solution is used, and the liquid is boiled before the addition of the grape-sugar, quinonephenolimide, $<^{C_6H_4}_{-O-}>N{\cdot}C_6H_4{\cdot}OH$, is produced by a similar reaction; the same change is also effected by boiling phenol-blue with soda.

α-Naphthol-blue, $C_{18}H_{16}N_2O$, is prepared by reducing nitroso-dimethylaniline hydrochloride with zinc-dust, and adding the product to an equimolecular proportion of *α*-naphthylamine hydrochloride dissolved in 500 parts of water. It forms bluish-violet, hard crystals.

V. H. V.

Para- and Ortho-nitroxanilic Acids and their Reduction. By O. Aschan (*Ber.*, **18**, 2936—2940).—*Paranitroxanilic acid*, $C_6H_6N_2O_5$, is obtained, together with a small quantity of the ortho-derivative, by the action of fuming nitric acid on oxanilic acid. It crystallises from water in long, pale yellow needles, containing 1 mol. H_2O. It melts at 210°. The *potassium* and *sodium salts* are sparingly soluble in cold water; the *ammonium salt* dissolves readily in alcohol. When paranitroxanilic acid is reduced, it yields paraphenylenediamine.

Orthonitroxanilic acid is best prepared by heating orthonitraniline with anhydrous oxalic acid for 40 minutes at 130—140°; the product is then washed with a little water and recrystallised from water. The acid separates in long, gold-coloured needles, melting at 112°. It is readily soluble in hot water, alcohol, and glacial acetic acid. The *alkali salts* are sparingly soluble in cold water and alcohol, and crystallise in yellow, lustrous needles. The *barium* and *silver salts* form colourless needles almost insoluble in water. The acid has already been obtained by v. Herff (*Annalen*, **209**, 367), who described it as "ethyl oxorthonitranilate." Tin and hydrochloric acid act on the acid with formation of *dihydroxyethenylphenylenediamine*, $C_8H_6N_2O_2$. This crystallises in long, slender needles with a glassy lustre melting at 280°; it is sparingly soluble in water, alcohol, and ether, insoluble in benzene, &c. It dissolves in alkali, with formation of unstable salts which are decomposed by carbonic anhydride. A similar compound was obtained by Hinsberg (Abstr., 1883, 323) from meta-nitroparoxaltoluidic acid.

N. H. M.

Isomeric Malontoluidic Acids. By L. Rügheimer and R. Hoffmann (*Ber.*, **18**, 2971—2975).—Malonparatoluidic acid has already been described (Abstr., 1884, 1023). The *calcium salt* (with $4\frac{1}{2}$ mols. H_2O) forms long, slender needles; the *barium* salt (with 5 mols. H_2O) forms lustrous prisms. The *silver*, *copper* (with 2 mols. H_2O), and *zinc salts* are also described. The *ethyl salt*

crystallises from alcohol in large, well formed, rhombic crystals, $a : b : c = 0{\cdot}9320 : 1 : ?$

Malonorthotoluidic acid, $C_6H_4Me{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}COOH$, is prepared in a manner similar to the para-acid (*loc. cit.*). It is readily soluble in water and alcohol, from which it crystallises in long, colourless needles; these become reddish when exposed to air. It melts at 138—143° with evolution of carbonic anhydride. The *calcium salt* (with 3 mols. H_2O) forms groups of small needles rather readily soluble in water; the *barium salt* (with 1 mol. H_2O) crystallises in broad needles, very readily soluble in water; the *copper salt* (with 2 mols. H_2O) crystallises in well-formed, lustrous, greenish-blue prisms. The *ethyl salt* forms long, narrow prisms melting at 73—74°.

Malonmetatoluidic acid, $C_6H_4Me{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}COOH$, forms large, lustrous plates which melt at 99—101°, and decompose only when heated to a still higher temperature. N. H. M.

Reaction of Benzaldehyde with Azobenzene. By T. Barzilovsky (*J. Russ. Chem. Soc.*, 1885, 366—368).—When azobenzene and benzaldehyde are heated with zinc chloride, a greenish-grey powder (m. p. 239°) is obtained and found to be identical with Schiff's benzilidene-benzidine (Abstr., 1878, 668). In the absence of zinc chloride, the reaction gives a different result; when heated in a sealed tube during three to four hours at 200°, the two compounds yield a dark brown, crystalline mass, which after purification forms white, glistening, nacreous plates, melting at 164°, easily soluble in alcohol and benzene, sparingly in ether, and very slightly in light petroleum. Its composition seems to indicate that it is a product of the direct union of benzaldehyde with azobenzene, $C_{12}H_{10}N_2(C_7H_6O)_2$. A further investigation of the compound will be made, as well as of the products which may be obtained from azobenzene and the three isomeric nitrobenzaldehydes, and from azobenzene and azotoluene and some saturated aldehydes. A. T.

Action of Alkyl Iodides on Amido-acids. By A. Michael and J. F. Wing (*Amer. Chem. J.*, **7**, 195—199).—Paramidobenzoic acid was dissolved in methyl alcohol, and an excess of caustic potash and methyl iodide (3 mols.) added, with addition of more potash from time to time. After removal of the methyl alcohol, the addition of acetic acid precipitated dimethylamidobenzoic acid; from the concentrated filtrate, hydriodic acid precipitated the hydriodide of the betaïne, $C_6H_4<\begin{matrix}NMe_3\\CO{\cdot}O\end{matrix}>$; the free base, its hydriodide and its platinochloride, are described. When ethyl iodide acts on paramidobenzoic acid in presence of ethyl alcohol, only ethyl diethylamidobenzoate is formed; no trace of a betaïne could be detected. Allyl iodide in alcoholic solution did not yield the corresponding betaïne, but only diallylparamidobenzoic acid melting at 127°; the corresponding allyl salt was not formed. The three iodides therefore show a gradual variation in their action. H. B.

Mononitro-derivatives of Par- and Met-acetamidobenzoic Acids and their Products of Reduction. By A. KAISER (*Ber.*, **18**, 2942—2952).—*Metanitroparacetamidobenzoic acid*,

$$COOH{\cdot}C_6H_3(NO_2){\cdot}NHAc\ [COOH : NO_2 : NHAc = 1 : 3 : 4],$$

is prepared by nitrating paracetamidobenzoic acid at a temperature below 10°, and subsequent purification of the product by means of its barium salt. It forms yellow plates melting at 220—221°, readily soluble in boiling alcohol, glacial acetic acid, and acetone, very sparingly soluble in cold water. Warm dilute hydrochloric acid saponifies it easily. The *barium salt* (with $6\frac{1}{2}$ mols. H_2O) forms yellow plates readily soluble in hot water; the *calcium salt* crystallises with 2 mols. H_2O in sparingly soluble, yellow needles. When a solution of the acid in glacial acetic acid is treated with tin *metaparanhydracetodiamidobenzoic acid*, $COOH{\cdot}C_6H_3{<}^{-\ N}_{NH}{>}CMe$, is formed. This compound crystallises with 1 mol. H_2O (which it loses at 100°), and melts with decomposition at 301—302°; it dissolves readily in boiling glacial acetic acid, less readily in hot alcohol, and is almost insoluble in ether, acetone, benzene, and chloroform. When heated above 160°, it gives off carbonic anhydride and yields anhydracetdiamidobenzene. The *hydrochloride* forms slender, white needles, very readily soluble in cold water; the *platinochloride* (with 2 mols. H_2O) crystallises in gold-coloured needles. The *potassium salt* forms colourless, microscopic needles.

Paranitrometacetamidobenzoic acid,

$$[COOH : NO_2 : NHAc = 1 : 4 : 3],$$

is obtained in a manner similar to the metanitro-derivative, and forms deep yellow plates which melt at 205—206°; it is readily soluble in boiling alcohol, glacial acetic acid, and acetone. The *barium salt* crystallises with 7 mols. H_2O, in long, slender, yellow needles; the *calcium salt*, with $7\frac{1}{2}$ mols. H_2O, forms nodular groups of yellow needles; both dissolve readily in boiling water. When saponified, the acid yields paranitrometacetamidobenzoic acid, melting at 298°. *Ethyl paranitrometamidobenzoate* crystallises in long, red needles melting at 139°, very readily soluble in ether, alcohol, acetone, &c. When paranitrometacetamidobenzoic acid is reduced, an anhydro-compound is formed identical with that obtained from metanitroparacetamidobenzoic acid.

Consecutive orthonitrometacetamidobenzoic acid was found in the mother-liquor obtained in the purification of paranitrometacetamidobenzoic acid; it forms colourless needles readily soluble in alcohol, glacial acetic acid, &c., and melts with decomposition at 240—241°. The *barium* (with 1 mol. H_2O) and *calcium* (with 6 mols. H_2O) *salts* are described. When saponified with baryta, it yields consecutive orthonitrometamidobenzoic acid melting at 156—157°.

N. H. M.

Action of Benzanilidoimide Chloride on Ethyl Sodomalonate. By F. JUST (*Ber.*, **18**, 2623—2631).—By this reaction about equal parts of ethyl mono- and di-anilbenzenylmalonate are formed.

Ethyl anilobenzenylmalonate, NPh : CPh·CH(COOEt)$_2$, is obtained from the product of the reaction, by diluting it with water, extracting with ether, evaporating the ethereal solution, and crystallising the residue from alcohol. It forms large, hard, monoclinic or triclinic crystals, which are strongly refractive, and show a blue fluorescence; it melts at 75°, and is insoluble in water, readily soluble in alcohol and ether. When heated with dilute hydrochloric acid in sealed tubes at 120°, it is converted into acetophenone, ethyl chloride, aniline hydrochloride, and carbonic anhydride.

Ethyl dianilbenzenylmalonate, C(CPh : NPh)$_2$(COOEt)$_2$, is contained together with ethyl malonate in the mother-liquor of the preceding compound; it can also be prepared by the action of sodium and benzanilidoimide chloride on the mono-compound. It crystallises in stellate groups of plates, and melts at 160°. When heated with dilute hydrochloric acid in sealed tubes at 150°, it yields benzoic and acetic acids, ethyl chloride, aniline hydrochloride, and carbonic anhydride.

Ethyl anilbenzenylethylmalonate, NPh : CPh·CEt(COOEt)$_2$, is obtained by the successive action of sodium and of benzanilidoimide chloride on ethylic ethylmalonate, as a colourless oil, which cannot be crystallised or distilled unaltered.

Benzanilide is formed by the action of aniline on the product of the reaction of benzoic chloride with ethyl sodomalonate. A. J. G.

Amidotoluenedisulphonic Acid. By H. Hasse (*Annalen*, **230**, 286—298).—Orthamidotoluenemetasulphonic acid,

$$NH_2·C_6H_3Me·SO_3H\ [Me : NH_2 : SO_3H = 1 : 2 : 5],$$

is converted into *amidotoluenedisulphonic acid*,

$$NH_2·C_6H_2Me(SO_3H)_2\ [Me : NH_2 : SO_3H : SO_3H = 1 : 2 : 3 : 5],$$

by the action of fuming sulphuric acid at 150—170°, or of chlorosulphonic acid at 160°. The disulphonic acid crystallises with 1½ mols. H_2O in colourless needles, which are soluble in alcohol and in water. The *normal barium* salt, $C_7H_7N(SO_3)_2Ba + 3H_2O$, crystallises in the triclinic system. It is freely soluble in water, but is precipitated from the solution by alcohol. The *acid* salt, $(SO_3H·C_7H_7N·SO_3)_2Ba + 3\frac{1}{2}H_2O$, forms microscopic needles soluble in water, but insoluble in alcohol. The *potassium* salt, $C_7H_7N(SO_3K)_2 + 2H_2O$, crystallises in monoclinic plates. The *sodium* salt forms tabular crystals containing 6 mols. H_2O. The *calcium* salt, $C_7H_7N(SO_3)_2Ca + 5H_2O$, forms long plates soluble in water, but not in alcohol. The *normal lead* salt, $C_7H_7N(SO_3)_2Pb + 2H_2O$, crystallises in colourless prisms. It is less soluble in water than the potassium salt. $(HSO_3·C_7H_7N·SO_3)_2Pb + 6\frac{1}{2}H_2O$ forms quadratic prisms. It is more soluble in water than the normal salt.

The disulphonic acid decomposes at 240°, yielding amidotoluenesulphonic and sulphuric acids. The diazo-compound is crystalline. The salts of amidotoluenedisulphonic acid are converted into diazotoluenedisulphonates by the action of nitrous acid. The *potassium* salt crystallises in anhydrous, yellow prisms. The *barium* salt,

$[C_7H_7N_2(SO_3)_2]_2Ba + 4H_2O$, is deposited from its aqueous solution on the addition of alcohol, in microscopic plates. The *lead* salt forms yellow, anhydrous plates.

Cresoldisulphonic acid is obtained in needles or plates by boiling an aqueous solution of the diazo-compound. It is freely soluble in water and alcohol. The *potassium* salt, $OH{\cdot}C_7H_5(SO_3K)_2 + 1\frac{1}{2}H_2O$, and *barium* salt, $OH{\cdot}C_7H_5(SO_3)_2Ba + 3\frac{1}{2}H_2O$, crystallise in needles. Diazotoluenedisulphonic acid is decomposed by boiling with absolute alcohol, yielding ethoxytoluenedisulphonic acid. It is also decomposed by hydrobromic acid, forming *bromotoluenedisulphonic acid*. The *potassium* salt, $C_7H_5Br(SO_3K)_2 + 4H_2O$, crystallises in plates, and the *barium* salt, $C_7H_5Br(SO_3)_2Ba + 1\frac{1}{2}H_2O$, in long, colourless needles, sparingly soluble in water. The *chloride* melts at 90°, and the *amide* at 237°. The bromine in the acid is replaced by hydrogen on treatment with sodium amalgam, but a better yield of toluenedisulphonic acid, $C_6H_3Me(SO_3H)_2$ [Me : SO_3H : SO_3H = 1 : 3 : 5], is obtained by the action of hydriodic acid on potassium diazotoluenedisulphonate. Toluenedisulphonic acid is an oily liquid. The ammonium and potassium salts are crystalline; the latter is insoluble in alcohol. The chloride, $C_7H_6(SO_2Cl)_2$, is deposited from ether in colourless prisms melting at 132°. The amide forms sparingly soluble plates, which melt at 230.

Attempts to prepare amidotoluenetrisulphonic acid were unsuccessful. W. C. W.

Two Disulphonic Acids of Paratoluidine. By L. Richter (*Annalen*, **230**, 313—333).—*Paramidotoluenedisulphonic acid*,

$$NH_2{\cdot}C_6H_2Me(SO_3H)_2 + 2H_2O,$$

can be prepared by the action of fuming sulphuric acid or of chlorosulphonic acid on paramidotoluenemetasulphonic acid. It forms a crystalline mass soluble in water, less soluble in alcohol. The *normal barium* salt, $NH_2{\cdot}C_7H_5(SO_3)_2Ba + 3H_2O$, crystallises in rhombic plates soluble in hot water, but insoluble in alcohol. The *acid barium* salt, $(SO_3H{\cdot}C_7H_7N{\cdot}SO_3)Ba + 3H_2O$, crystallises in needles. It dissolves freely in hot water. *Potassium amidotoluenedisulphonate*, $NH_2{\cdot}C_7H_5(SO_3K)_2 + 2H_2O$, is deposited in pointed prisms from an aqueous solution on the cautious addition of alcohol. The normal lead salt forms anhydrous, silky needles, soluble in water. The acid lead salt forms white needles. It is less soluble than the normal salt. Paramidotoluenedisulphonic acid is decomposed by heat at 200°, or by the action of water at 140°, into sulphuric and paramidotoluenemetasulphonic acids. The diazo-compound of the disulphonic acid is exceedingly soluble in water, but is neither dissolved nor decomposed by alcohol. The potassium, barium, and lead salts of this acid are anhydrous. They are decomposed by boiling with water, yielding salts of paracresoldisulphonic acid. The free acid forms needle-shaped crystals, which are freely soluble in water and alcohol. *Barium paracresoldisulphonate*, $OH{\cdot}C_7H_5(SO)_2Ba + 4H_2O$, crystallises in flat needles, soluble in water. The *potassium* salt, which crystallises in

plates, and the lead salt, $OH{\cdot}C_7H_5(SO_3)_2Pb + 3H_2O$, are precipitated from their aqueous solutions by alcohol.

The *dinitroparacresol* obtained from the amidodisulphonic acid crystallises in lemon-coloured needles. It melts at 82·5°, and dissolves freely in alcohol, sparingly in water. The potassium, barium, and silver salts are crystalline.

Barium and potassium *parabromotoluenedisulphonates*,

$$C_7H_5Br(SO_3)_2Ba + 6H_2O, \text{ and } C_7H_5Br(SO_3K)_2 + H_2O,$$

form silky needles soluble in water.

The *sulphonic chloride* forms thick prisms melting at 133°. It is freely soluble in ether. On cooling its hot aqueous solution, the *amide* is deposited in colourless prisms soluble in hot water and in alcohol. It melts above 240°.

Pariodotoluenedisulphonic acid, $C_7H_5I(SO_3H)_2$, forms needle-shaped crystals freely soluble in alcohol and water. The *barium* salt, $C_7H_5I(SO_3)_2Ba + 6H_2O$, and the *potassium* salt, $C_7H_5I(SO_3K)_2 + 2H_2O$, are soluble in water, but insoluble in alcohol. The sulphonic chloride forms quadratic prisms. It melts at 143°; but if it is allowed to solidify and is then reheated, it melts at 126°. The amide melts at 130—132°, and is soluble in alcohol.

The *toluenedisulphonic acid*, $C_7H_6(SO_3H)_2$, obtained by the action of sodium amalgam on an aqueous solution of potassium iodotoluenedisulphonate, is identical with the acid described by Hakansson, (*Ber.*, **5**, 1084).

Hydrazinetoluenedisulphonic acid, $N_2H_3{\cdot}C_7H_5(SO_3H)_2$, is a crystalline compound dissolving freely in alcohol and in water. The acid barium salt crystallises in plates containing $2\frac{1}{2}$ mols. H_2O.

II. *Paramidotoluenedisulphonic acid*, $NH_2{\cdot}C_6H_2Me(SO_3H)_2 + 2\frac{1}{2}H_2O$, forms silky needles freely soluble in water, less soluble in alcohol. The *normal barium* salt crystallises in plates containing 1 mol. H_2O. It is sparingly soluble in water. The *acid barium* salt crystallises with $1\frac{1}{2}$ or $\frac{1}{2}$ mol. H_2O. The *potassium* salt contains 2 mols. H_2O. It is freely soluble in water, but insoluble in alcohol. The free acid decomposes at 290°, yielding paramido-orthosulphonic and sulphuric acids. W. C. W.

Nitrotoluidinesulphonic Acid. By G. Foth (*Annalen*, **230**, 298—313).—The best yield of nitrotoluidinesulphonic acid,

$$NO_2{\cdot}C_6H_2Me(NH_2){\cdot}SO_3H \; [Me : NO_2 : NH_2 : SO_3H = 1 : 2 : 4 : 5],$$

is obtained by the action of chlorosulphonic acid on nitrotoluidine at 160°. The crude product is dissolved in ammonia, and the free acid liberated from the ammonium salt by the addition of hydrochloric acid. The pure acid is deposited from its aqueous solution in pale-yellow needles which darken on exposure to the air. It is sparingly soluble in alcohol and in cold water. *Potassium nitrotoluidinesulphonate*, $C_7H_7N_2O_2{\cdot}SO_3K + H_2O$, crystallises in needles or prisms of an orange colour, and the ammonium salt in golden needles or prisms. Both salts are sparingly soluble in cold water. The *barium* salt, $(C_7H_7N_2O_2{\cdot}SO_3)_2Ba + 4H_2O$, forms yellowish-red prisms. The lead

and silver salts are also sparingly soluble in cold water; the former crystallises in red needles, and the latter in glistening white prisms.

The diazo-compound, $NO_2 \cdot C_6H_2Me<^{\cdot SO_3 \cdot}_{N:N>}$, is prepared by adding dilute sulphuric acid to a solution of potassium nitrite and nitrotoluidine sulphonate. It is converted into nitrotoluenesulphonic acid by the action of absolute alcohol at 100°.

Nitrotoluenesulphonic acid, $NO_2 \cdot C_6H_3Me \cdot SO_3H$ [Me : NO_2 : SO_3H = 1 : 2 : 5], and its salts are very soluble in water, and crystallise with difficulty. The potassium salt forms thick prisms of a reddish-yellow hue. The sulphonic chloride is deposited from ether in thick prisms melting at 50°. It is freely soluble in ether and in glacial acetic acid. The *amide* forms glistening needle-shaped crystals, which are freely soluble in alcohol. It melts at 133·5°. When reduced with ammonium sulphide, nitrotoluenesulphonic acid yields a *toluidinesulphonic acid*, $NH_2 \cdot C_6H_3Me \cdot SO_3H$ [Me : NH_2 : SO_3H = 1 : 2 : 5], which appears to be identical with the acid described by Pagel (this Journal, 1875, 897), and by Nevile and Winther (Trans., 1880, 626).

Iodotoluidinesulphonic acid, $NH_2 \cdot C_7H_7I \cdot SO_3H$, prepared by the action of hydriodic acid on the diazo-compound of nitrotoluidinesulphonic acid, crystallises in needles. It is sparingly soluble in water. The barium salt crystallises in rhombic plates which are freely soluble in water.

Toluylenediaminesulphonic acid, $C_6H_2Me(NH_2)_2 \cdot SO_3H$ [1 : 2 : 4 : 5], is obtained by the action of stannous chloride on nitrotoluidinesulphonic acid. It is a crystalline substance, and unites with acids as well as with bases, forming crystalline compounds: for example,

$$C_7H_5(NH_2)_2 \cdot SO_3H,HCl + H_2O; \quad C_7H_5(NH_2)_2 \cdot SO_3K + H_2O.$$

The barium salt contains $5\frac{1}{2}$ mols. H_2O.

Nitrotolylhydrazinesulphonic acid,

$$NO_2 \cdot C_6H_2Me(N_2H_3) \cdot SO_3H \text{ [Me : } NO_2 : N_2H_3 : SO_3H = 1 : 2 : 4 : 5],$$

crystallises in quadratic plates. The *barium* salt forms long, yellow prisms containing 4 mols. H_2O. It is freely soluble in hot water, but only sparingly soluble in cold. W. C. W.

Orthamidometaxylenesulphonic Acid. By J. Sartig (*Annalen*, **230**, 333—345).—The author confirms Jacobsen's statements (Abstr., 1883, 593) regarding orthamidometaxylenesulphonic acid and its salts, with the exception that he finds that the barium salt contains 2 mols. H_2O, whilst Jacobsen found only 1 mol. H_2O. The diazo-compound crystallises in microscopic rhombic plates. It is decomposed by hydrobromic acid, yielding a bromo-xylenesulphonic acid, $C_6H_2Me_2Br \cdot SO_3H$ [Me : Me : Br : SO_3H : 1 : 3 : 6 : 4], which has been described by Wedding (*Ber.*, **11**, 1062). By decomposing the diazo-compound with water, *xylenolsulphonic acid*,

$$OH \cdot C_6H_2Me \cdot SO_3H \text{ [Me : Me : OH : } SO_3H = 1 : 3 : 6 : 4],$$

is obtained in needle-shaped crystals which are freely soluble in water and alcohol. The aqueous solution gives a violet coloration with

ferric chloride, which turns green on the addition of alcohol. The *barium*, $(OH{\cdot}C_8H_8{\cdot}SO_3)_2Ba + H_2O$, and *lead*, $(OH{\cdot}C_8H_8SO_3)_2Pb + 2H_2O$, salts crystallising in needles, and the anhydrous potassium salt crystallising in rhombic plates, are easily soluble in water. Absolute alcohol decomposes the diazo-compound, forming *ethoxy-xylenesulphonic acid*, $OEt{\cdot}C_6H_2Me_2{\cdot}SO_3H$ [Me : Me : OEt : SO_3H = 1 : 3 : 6 : 4]. This acid crystallises in microscopic, rhombic plates, which are freely soluble in alcohol and in water. The *barium* salt contains 3 mols. H_2O; it is soluble in water and in alcohol.

Nitramido-xylenesulphonic acid, $NH_2{\cdot}C_6HMe_2(NO_2){\cdot}SO_3H$, prepared by the action of a mixture of strong nitric and sulphuric acids on amidoxylenesulphonic acid, crystallises in colourless needles. It is sparingly soluble in water and in alcohol. The *potassium* and *barium* salts crystallise in rhombic plates containing $1\frac{1}{2}$ mols. H_2O. They dissolve freely in water; the barium salt is but sparingly soluble in alcohol. *Lead nitro-xylidinesuphonate*, $NH_2(C_8H_7SO_3)_2Pb + H_2O$, forms silky needles soluble in water. The diazo-compound crystallises in quadratic plates. It is decomposed by boiling water, yielding *nitro-xylenol-sulphonic acid*. This acid is freely soluble in water and alcohol. The *barium* and *lead* salts crystallise with 3 mols. H_2O. They are more soluble in water than in alcohol.

Bromonitro-xylenesulphonic acid, $NO_2{\cdot}C_6HMe_2Br{\cdot}SO_3H$, crystallises in rhombic plates, which dissolve freely in alcohol and water. The *barium* salt, $(NO_2{\cdot}C_8H_7Br{\cdot}SO_3)_2Ba + 3\frac{1}{2}H_2O$, forms needle-shaped crystals soluble in hot water and in alcohol. The *potassium* salt contains 1 mol. H_2O. It forms yellow prisms, and resembles the barium salt in solubility. The *potassium* and *barium* salts of the ethoxy-nitrosulphonic acid are insoluble in alcohol, but soluble in warm water.

Diamido-xylenesulphonic acid, $C_6HMe_2(NH_2)_2{\cdot}SO_3H$, obtained by the action of tin and hydrochloric acid on nitramido-xylenesulphonic acid, crystallises in prisms. It is soluble in water, but insoluble in alcohol, and forms crystalline compounds with acids and with bases. The *barium* salt crystallises in microscopic, rhombic plates, the *potassium* and *lead* salts in prisms. The first contains $3\frac{1}{2}$ mols. H_2O, the potassium salt 1 mol. H_2O, and the lead salt is anhydrous.

W. C. W.

Condensation Products of Isatin. By A. Baeyer and M. J. Lazarus (*Ber.*, **18**, 2637—2643).—Fresh analyses of indophenine and its dibrom-derivative lead to the formulæ $C_{12}H_7NOS$ and $C_{12}H_5Br_2NOS$ for these compounds.

Whilst benzene does not seem to unite with isatin, toluene reacts readily with it in presence of sulphuric acid. *Toluisatin*,

$$NH<^{C_6H_4}_{CO}>C(C_7H_7)_2,$$

so obtained, crystallises in lustrous, colourless needles, melts at 200—201°, is readily soluble in alcohol, ether, and benzene, sparingly in light petroleum, insoluble in water, acids, and alkalis. The *acetyl*-derivative, $C_{24}H_{21}NO_2$, crystallises in thin, colourless needles, melts at

142—143°, and yields toluisatin when boiled with alkalis. The *ethyl*-derivative, $C_{24}H_{23}NO_2$, prepared by heating toluisatin with sodium ethoxide and ethyl iodide, or by the condensation of ethylpseudoisatin with toluene, crystallises in nearly colourless plates, and melts at 108°. From these results, it follows that toluisatin must be regarded as a pseudoisatin-derivative, and that in the condensation of isatin with toluene a conversion of isatin into pseudo-isatin must have occurred. *Tolubromisatin*, $C_{22}H_{18}BrNO$, prepared from toluene and bromisatin, crystallises in colourless needles, and melts at 235°; the acetyl-derivative crystallises in needles, and melts at 156°.

Phenolisatin, $NH<^{C_6H_4}_{CO}>C(C_6H_4\cdot OH)_2$, is prepared by dissolving isatin in an excess of phenol and adding sulphuric acid, with constant agitation, until the colour of the isatin has disappeared. It crystallises in slender, white needles, melts at 220°, is practically insoluble in water, sparingly soluble in benzene and chloroform, readily in ether and in alkalis. When potassium ferricyanide is added to an alkaline solution, a deep reddish-violet coloration is produced. The acetyl-derivative, $C_{22}H_{17}NO_4$, crystallises in colourless needles, and melts at 185°.

Anisoïlisatin, $C_{22}H_{19}NO_3$, is obtained by condensation from a mixture of anisoïl with excess of isatin. It crystallises in colourless needles, melts at 65°, is soluble in most solvents, but not in alkalis.

Dimethylanilinisatin, $NH<^{C_6H_4}_{CO}>(C_6H_4\cdot NMe_2)_2$, is prepared by heating isatin with an excess of dimethylaniline and zinc chloride on the water-bath for 5—6 hours. It crystallises in colourless, lustrous, well-formed prisms, melts at 234°, is insoluble in water and alkalis, sparingly soluble in ether, alcohol, and light petroleum, readily soluble in dilute acids. When oxidised, it yields a product that seems to be identical with Fischer and Schmidt's orthamidobenzaldehyde-green (Abstr., 1884, 1315). A. J. G.

Simultaneous Oxidation and Reduction by Means of Hydrocyanic Acid. By A. Michael and G. M. Palmer (*Amer. Chem. J.*, **7**, 189—194).—Benzil, when treated with alcoholic potassium cyanide and concentrated hydrochloric acid is converted almost quantitatively into benzaldehyde and ethyl benzoate. Strong aqueous hydrocyanic acid at 200° effects the same change. Benzoquinone, when treated with alcoholic potassium cyanide and hydrochloric acid is converted into benzoquinol, and an oily liquid not fully examined, but probably ethylbenzoquinol. Benzoïn is converted into benzaldehyde and ethyl benzoate. Benzaldehyde when heated at 200° with alcohol and hydrocyanic acid yields benzoic acid and ethyl benzoate, probably also benzyl alcohol. The work is being continued. H. B.

Nitronaphthoic Acids. By A. G. Ekstrand (*Ber.*, **18**, 2881—2887).—A discussion of the constitution of the nitronaphthoic acids obtained by the nitration of α-naphthoic acid, and melting at 215° and 239° respectively (Abstr., 1885, 548). Both acids are converted into dinitronaphthalenes, the former yielding the β-, the latter the

α-compound. As the α-dinitronaphthalene yields mononitrophthalic acid [NO_2 : COOH : COOH = 1 : 2 : 3] on oxidation, the NO_2-groups as also the NO_2- and COOH-groups in the nitronaphthoic acid are in the positions 1 : 4′; then in the β-dinitronaphthane and its corresponding nitronaphthoic acid, the groups will be in the position 1 : 1′.

The nitro-acid melting at 239° can be converted into a chloronaphthoic acid melting at 245°, which on nitration yields a nitrochloronaphthoic acid, melting at 225° and crystallising in prismatic needles; its ethyl salt crystallises in tables melting at 125°. On reduction, the acid is converted into an anhydride, $C_{10}H_3Cl<\begin{matrix}NH\\CO\end{matrix}>$, crystallising in yellow needles, and melting at 270°. The ready formation of this anhydride points to the contiguity of the α-positions of the nitro- and carboxyl-groups respectively. V. H. V.

α-Naphthol-β-sulphonic Acid. By A. Claus and M. Knyrim (*Ber.*, **18**, 2924—2930).—This acid is formed when α-naphthol dissolved in glacial acetic acid is sulphonated at a temperature below 75°. It forms long, slender, deliquescent needles, melting at 90° (uncorr.). A dilute solution of the acid decomposes when boiled, with separation of α-naphthol. The *sodium salt* forms white, lustrous plates readily soluble in water; the *potassium salt* crystallises in colourless needles, also readily soluble in water. The *barium* and *lead salts* (each with 1 mol. H_2O) were prepared. When the sodium salt is treated with phosphorus pentachloride in presence of chloroform, *dichloronaphthol*, $C_{10}H_6Cl_2O$ [OH : Cl : Cl = 1 : 2 : 3], is formed; this compound sublimes in white needles, melting at 101° (uncorr.), and is readily soluble in chloroform, alcohol, ether, benzene, &c. The *sodium* and *barium salts* are readily soluble. Phosphorus pentachloride acts on dichloronaphthol at 140°, yielding *trichloronaphthalene* [Cl_3 = 1 : 2 : 3] melting at 90°, and probably identical with that obtained by Faust and Saame (this Journal, 1872, 64), and that of Atterberg (this Journal, 1876 [ii], 516). When dichloronaphthol is heated with dilute nitric acid at 200°, it yields phthalic acid. Chromic anhydride converts it into dichloronaphthaquinone, [O : Cl_2 : O = 1 : 2 : 3 : 4]. N. H. M.

Camphoronic Acid. By J. Bredt (*Ber.*, **18**, 2989—2990).—Camphoronic acid has the formula $C_9H_{14}O_6$, and not $C_6H_{10}O_4$, that ascribed to it by Rudzinski (*Inaug. Diss.*, Würzburg, 1879). When slowly distilled it loses water and carbonic anhydride, yielding isobutyric acid, and the anhydride of a new acid, $C_6H_{12}O_4$(?), melting at 135°. The *calcium salt*, $C_7H_{10}O_4Ca + 2\frac{1}{2}H_2O$, and the *silver salt*, $C_7H_{10}O_4Ag_2$, were prepared. N. H. M.

Note.—The formulæ of the new acid and its salts are given as printed in the original.

Fluorescent Constituent of Atropa Belladonna. By H. Paschkis (*Arch. Pharm.* [3], **23**, 541—543).—10 kilos. of ripe belladonna berries were extracted with strong alcohol, the solution evaporated to dryness, the residue taken up with hot water, and the acid liquid thus obtained, agitated with chloroform. The residue

obtained on evaporation of the chloroform extract was recrystallised from hot concentrated alcohol, from 40 per cent. alcohol, and finally from water. When pure, the substance crystallises in yellowish-white, slender needles, seemingly rhombic pyramids; it melts at 197—198°. It dissolves sparingly in cold water and in ether, more easily in hot water, chloroform, and in concentrated alcohol, and very easily in hot alcohol, ethyl acetate, acetic acid, and alkalis. Amyl alcohol and benzene extract it from its aqueous solution. The aqueous solution reacts faintly acid; the aqueous, alkaline, and especially the ammoniacal and alcoholic solutions, show a splendid blue fluorescence. The fluorescence disappears on adding acids, but alkalis cause its reappearance. The sulphuric acid solution when nearly neutralised with ammonia shows a fine purple-violet colour by reflected light, but is colourless by transmitted light. The aqueous solution gives a beautiful blue precipitate with gold chloride, and a green one with iron chloride; alkaline copper solution and ammoniacal silver nitrate solution are reduced on warming. In slightly concentrated nitric acid, the substance dissolves with a yellow colour, which becomes blood-red on the addition of ammonia (reaction of æsculin according to Sonnenschein). The substance seems to be identical with scopoletin, obtained by Eijkman from *Scopolia japonica* (Abstr., 1884, 404). The yield is only about 0·001 per cent. J. T.

A New Nitrogenous Constituent of Plants. By E. Schulze and E. Bosshard (*Zeit. physiol. Chem.*, **10**, 80—89).—The authors give the name *vernine* to this substance, and prepare it as follows; the young plants are dried, and extracted with hot water; the extract is precipitated by lead acetate, and then by mercuric chloride. The precipitate produced by the latter reagent is collected, washed with cold water, and treated with hydrogen sulphide, the filtrate is neutralised with ammonia, and concentrated in a water-bath. On cooling, a jelly-like amorphous substance and asparagine crystals appear, these are collected, and the amorphous substance dissolved in hot water; on cooling this solution, crystals of vernine form. Vernine may be also separated from asparagine by fractional crystallisation, vernine crystallising first. It crystallises in long, thin prisms of the formula $C_{16}H_{20}N_8O_8 + 3H_2O$; gives precipitates with silver nitrate, mercuric chloride, phosphotungstic acid, and with copper acetate. It does not dissolve cupric oxide; it is slightly soluble in dilute hydrochloric and dilute nitric acids. On evaporating the nitric acid solution to dryness and adding ammonia, the residue is turned reddish-yellow. The silver compound has the formula $C_{16}H_{18}Ag_2N_8O_8$. Guanine is formed amongst other products when vernine is heated with hydrochloric acid. Vernine occurs in *Vicia sativa*, *Trifolium pratense*, ergot of rye, *Medicago sativa*, *Pinus silvestris*, &c.; the quantity present in ergot being 0·1 per cent., in vetch 0·05 per cent. of the dried plant. W. D. H.

Action of Phosphorus Pentachloride on Santonin. By B. Pawlewski (*Ber.*, **18**, 2900—2901).—If equal molecular proportions of santonin and phosphorus pentachloride are heated together, and the

crude product crystallised from ether, a *monochloro-derivative*, $C_{15}H_{17}ClO_2$, is obtained in the form of small crystals melting at 125°, readily soluble in benzene, sparingly soluble in alcohol.

If two molecules of phosphorus pentachloride are used, a dichloro-derivative is formed; this can best be crystallised from a mixture of benzene and petroleum. It is a pale yellow substance, melting at 182°, insoluble in water, sparingly soluble in alcohol.

Thus the two hydroxyl groupings in santonin are successively replaced by chlorine, but it appears probable that these groups are different in function. V. H. V.

Reactions of Iodine Chloride with Alkaloïds. By A. Dittmar (*Ber.*, **18**, 1612—1622).—When quinoline is treated with iodine chloride, *quinoline-chloriodide*, C_9H_7NICl, is obtained as a yellow precipitate; this is acted on by ammonia, yielding a dark green compound, $C_9H_7NH_2I$, which when warmed with alcohol decomposes with evolution of nitrogen and ammonia, and formation of quinoline and of a compound, $C_9H_7NI_2$. It is therefore probably a molecular compound. This characteristic yellow precipitate, giving the ammonia reaction above described, is obtained by the action of iodine chloride on all substances containing pyridine nuclei, with the exception of a few quinoline-derivatives. Several chloriodides are described. Substitution in the pyridine-ring does not prevent the reaction from taking place, but influences the results; for instance, *quinaldine chloriodide* reacts with ammonia only when warmed. Hydroxyquinolines, hydroxylated in the benzene-ring, react differently with iodine chloride; the products do not react with ammonia. The author expects, with the help of this difference of behaviour, to be able to determine the presence or absence of substitution in certain directions in the alkaloïds.

The reactions of the alkaloïds with iodine chloride are described. All alkaloïds which react with iodine chloride and yield the characteristic bright yellow precipitate which gives the ammonia reaction, contain one or more pyridine nuclei, the number of the latter, corresponding, as a rule, with the number of halogen-groups in the product. N. H. M.

Method for Determining Positions in the Pyridine Series. By A. Ladenburg (*Ber.*, **18**, 2967—2969).—The fact that cinchomeronic acid, when heated, yields two monocarboxylic acids (nicotic and isonicotic acids) excludes the constitution $\alpha\alpha'$ and $\beta\beta'$. The position $\alpha\beta$, as belonging to quinolinic acid which when heated yields nicotic acid, is excluded, as is also the position $\alpha\beta'$. The only positions which now remain are $\alpha\gamma$ and $\beta\gamma$, from which it follows that either nicotic or isonicotic acid has the carboxyl in the γ-position; nicotic acid must, however, have the carboxyl-group in the α- or β-position, as it can be obtained from quinolinic acid: hence isonicotic acid has the constitution, [N : COOH = 1 : 4].

When cinchomeronic acid is reduced, cinchonic acid is formed; this, when distilled yields pyrocinchonic anhydride, the acid corresponding with which can be obtained from α-dichloropropionic acid, and must therefore contain adjacent carboxyl-groups. In nicotic acid,

the carboxyl must therefore have the β-position, and in picolinic acid the only other position: namely, the α-position. N. H. M.

Ethylpyridine and Ethylpiperidine. By A. Ladenburg (*Ber.*, **18**, 2961—2967; compare Abstr., 1885, 992).—The product obtained by heating pyridine ethiodide at 290° yields three bases: α-ethylpyridine, γ-ethylpyridine, and α-γ-diethylpyridine.

α-Ethylpyridine forms the chief product; it boils at 150°. The *platinochloride* melts at 168—170°, and dissolves readily in water; the *hydrochloride* melts at about 110°. When oxidised, the base yields picolinic acid, and a small quantity of isonicotic acid (from the γ-derivative present as impurity). The base when reduced yields α-ethylpiperidine, which was previously prepared (Abstr., 1884, 1054) but described as γ-ethylpiperidine. The *platinochloride* melts at 178°.

γ-Ethylpyridine boils at 164—166°. Sp. gr. = 0·9592 at 0°; 0·9358 at 20°. It is sparingly soluble in water, and has an offensive odour. Its reactions resemble those of the α-compound. The *platinochloride* crystallises in well-formed plates melting at 208°. The *gold salt* forms gold-coloured, lustrous prisms, which melt at 138°. The *picrate* melts at 163°. When oxidised the base yields only isonicotic acid. When reduced, a *base*, $C_7H_{15}N$, is formed, which boils at 156—158°; this is sparingly soluble in water, and has a disagreeable odour resembling that of piperidine. Sp. gr. = 0·8759 at 0°. The *platinochloride* forms yellow plates sparingly soluble in cold water; it melts at 173—174°. The *gold salt* melts at 105°.

α-γ-Diethylpyridine, $C_9H_{13}N$, is formed only in small quantities; it boils at 187—188°, has an unpleasant odour, and is sparingly soluble in water. When oxidised it yields α-γ-lutidinic acid.

N. H. M.

Metachloroquinoline. By W. La Coste (*Ber.*, **18**, 2940—2942).—The author has found that the metachloroquinoline previously examined by him (Abstr., 1885, 792) is a mixture of chloroquinoline melting at 31—32°, and metachloroquinoline, which is a liquid at the ordinary temperature and boils at about 257°. The *dichromate* of the solid derivative forms long, slender, bright yellow needles which melt with decomposition at 165°; *metachloroquinoline dichromate* crystallises in nodular-groups of very small needles melting at 109°. The solid base is acted on by nitric acid with formation of a compound previously described as α-nitro-metachloroquinoline (compare Abstr., 1884, 1196); metachloroquinoline, when nitrated, yields β-nitrometachloroquinoline. N. H. M.

Toluquinolines Substituted in the Pyridine-ring. By L. Rügheimer and R. Hoffmann (*Ber.*, **18**, 2979—2989).—*α-β-γ*-Trichloroparatoluquinoline (methyltrichloroquinoline) (Abstr., 1884, 1023) can also be prepared by the action of phosphoric chloride on paratoluidine malonate dissolved in dry benzene; the product is treated with water and with soda, and distilled with steam. Besides trichlorotoluquinoline, dichloracetoparatoluide is obtained; the two substances are separated by means of concentrated hydrochloric acid.

Trichlorotoluquinoline is a feeble base readily soluble in strong acids, but is precipitated by adding water.

β-γ-Dichloroparatolucarbostyril, $C_{10}H_7NCl_2O$ [Me : Cl_2 = 3 : 3′ : 4′], is obtained by heating trichlorotoluquinoline with dilute hydrochloric acid for five hours at 180°; it forms slender needles insoluble in water, sparingly soluble in alcohol and ether, and melts at 290—292°, becoming brown at the same time. It has both feeble acid and basic properties. The *potassium salt* forms lustrous plates which are decomposed by water. When a solution of the base in sulphuric acid is saturated with nitrous acid, being kept cold all the while, and the product poured into water, *β-γ-dichlorodinitroparatolucarbostyril*, $C_{10}H_5NCl_2(NO_2)_2$, is formed. This crystallises from alcohol in long, lemon-coloured needles which melt at 186°.

Monochlorodiethoxyparatoluquinoline,

$$C_9NH_3MeCl(OEt)_2 \text{ [OEt : OEt = 2′ : 3′ or 4′]},$$

is prepared by heating trichlorotoluquinoline with a solution of sodium in anhydrous alcohol for two hours at 100°, and then for four hours at 130°; the product is filtered and washed with water. It forms long, colourless needles melting at 70·5—71·5°.

Dichlorohydroxyorthotoluquinoline,

$$C_9NH_3MeCl_2{\cdot}OH \text{ [Me : } Cl_2 \text{ : OH = 1 : 2′ : 3′ : 4′]},$$

is obtained by the action of phosphoric chloride on hydrogen orthotoluidine malonate, and forms microscopic needles which melt at 245°; it is sparingly soluble in water, alcohol, and glacial acetic acid. It dissolves in dilute, but more readily in concentrated acids; it also dissolves in carbonates. When heated with phosphoric chloride for 1½ hours at 125°, it yields 2′ : 3′ : 4′ *trichlororthotoluquinoline*, $C_9NH_3Cl_3Me$, which resembles in appearance trichloroquinoline and trichloroparatoluquinoline; it melts at 111—112·5°. It dissolves readily in concentrated hydrochloric acid, and is precipitated by the addition of water. Dilute hydrochloric acid acts on it at 180° with formation of *dichlororthotolucarbostyril*,

$$C_9NH_3MeCl_2{\cdot}OH \text{ [Me : } Cl_2 \text{ : OH = 1 : 3′ : 4′ : 2′]}.$$

This compound melts at 287—288°, and when strongly heated, sublimes; it is insoluble in water, sparingly soluble in boiling alcohol, but dissolves readily in alcoholic potash.

Hydroxychlororthotolucarbostyril,

$$C_9NH_3MeCl(OH)_2 \text{ [Me : Cl : } (OH)_2 \text{ = 1 : 3′ : 2′ : 4′]},$$

is formed when 4′ : 2′ : 3′ hydroxydichlororthotoluquinoline is heated with dilute hydrochloric acid for five hours at 160°. It crystallises in lustrous plates melting at 276—277°, and is readily soluble in glacial acetic acid, in ammonia, and in alkaline carbonates. It is insoluble in water, and sparingly soluble in alcohol.

Dichloracetorthotoluide, $C_6H_4Me{\cdot}NH{\cdot}CO{\cdot}CHCl_2$, prepared from orthotoluidine malonate, crystallises in needles, which are very readily soluble in alcohol and ether, sparingly soluble in light petroleum. It dissolves slowly in dilute soda. When warmed with caustic alkali, it

decomposes, giving off an odour of isonitriles. Phosphoric chloride acts on it with formation of a mixture of di- and tri-chlorinated quinolines.

Dichloracetometatoluide, $C_6H_4Me{\cdot}NH{\cdot}CO{\cdot}CHCl_2$, forms slender, colourless plates with silky lustre, melting at 98—100°. It is decomposed when warmed with alkaline carbonates, and yields an oil having the powerful odour of isonitriles. N. H. M.

Formation of Quinoline-derivatives by the Action of Phosphoric Chloride on the Malonates of Primary Aromatic Bases. By L. Rügheimer (*Ber.*, **18**, 2975—2978).—A discussion of the theoretical bearings of the results described by the author in other papers (Abstr., 1884, 1050, and preceding Abstract).

Formation of Quinolines from Meta-substituted Amines. By L. Meyer (*Ber.*, **18**, 2902—2903).—This paper is a preliminary notice regarding the production from paraxylidene sulphate of a dimethylquinoline boiling at 265° under 736 mm. pressure and of sp. gr. 1·070 at 21°. It is converted into a methylquinolinecarboxylic acid by nitric acid. This acid, when heated, loses carbonic anhydride, and yields a methylquinoline, possibly identical with that obtained from metatoluidine. V. H. V.

Synthesis in the Quinoline Series. By F. Just (*Ber.*, **18**, 2632—2635).—When ethyl anilbenzenylmalonate,

$$PhN{:}CPh{\cdot}CH(COOEt)_2$$

(this vol., p. 149), is heated at 150°, it is decomposed into ethyl alcohol and *ethyl phenylhydroxylquinolinecarboxylate*,

$$OH{\cdot}C_9NH_4Ph{\cdot}COOEt\,[Ph:COOEt:OH = 2':3':4'];$$

it is colourless, crystalline, and melts at 262°. The *free acid* is obtained by heating the ethyl salt with hydrochloric acid at 120°, and melts at 232°; on further heating, it is converted into a hydroxyquinoline which, when distilled with zinc-dust, yields the known α-phenylquinoline [Ph = 2'], thus confirming the constitution deduced from the method of formation. The author intends to apply this method to the preparation of substituted quinolines, preparing in the first place substituted anilbenzenylmalonates by the action of ethyl sodomalonate or its substitution-derivatives on substituted benzanilimide chlorides, and thus obtaining quinoline-derivatives of known structure. A. J. G.

Reduction of Nicotine. By A. Liebrecht (*Ber.*, **18**, 2969—2970).—*Dipiperidyl*, $C_{10}H_{20}N_2$, is obtained by reducing nicotine in alcoholic solution with sodium. The *platinochloride* forms dark red crystals which melt at 202°; the *hydrochloride*, *aurochloride*, and *picrate* are described. *Dinitrosodipiperidyl*, $NO{\cdot}C_5NH_9{\cdot}C_5NH_9{\cdot}NO$, is prepared by the action of sodium nitrite on the base. N. H. M.

Action of Caustic Alkalis on Cinchonine. By A. Krakau (*J. Russ. Chem. Soc.*, 1885, 356—366).—A mixture of cinchonine

and pure soda was heated in a flask and, as soon as the temperature had reached 170—190°, a current of superheated steam passed through the apparatus, the reaction being conducted generally at 195—210°. A yellowish, optically active oil distils over with the steam. This product, a mixture of different substances, was redistilled with steam, when an optically inactive oil passed over, whilst a viscous heavy oil remained, which contained some cinchonine, but not enough to account for the optical activity of the original product, and another substance not yet fully investigated. The inactive oil, on being redistilled, passed over between 240° and 265°; its alcoholic solution was treated with alcoholic sulphuric acid, when crystallisation at once took place. The pink crystals, separated from the brownish-red mother-liquor, after being boiled with absolute alcohol and repeatedly crystallised from acetic acid, melt at 228—229°; they are insoluble in ether, chloroform, and benzene, easily soluble in water, and were found to be almost pure lepidine bisulphate. The pink substance becomes colourless by treatment with animal charcoal, the melting point remaining unchanged. In the brown mother-liquor, quinoline bisulphate (m. p. 163·5—164·5°) was found.

The bases lepidine and quinoline, and some of their salts, were prepared from the bisulphates. As the former was obtained in a state of greater purity than by any other investigator, a more detailed description of it is given: it is an oil distilling at 205·5° (bar. 746·7 mm.), of sp. gr. 1·0995 at 0° and 1·0862 at + 20°; the author prepared the dichromate (begins to decompose at 136—138°), the picrate melting at 212—213°, the platinochloride, and the aurochloride melting at 188—190°.

The optically active oil formed in the reaction simultaneously with lepidine and quinoline (resembling cinchonine in its properties) seems to be produced in the early stages of the reaction of caustic alkalis on cinchonine; indeed, if the reaction is carefully conducted without the use of superheated steam, the oil is found in the product without any lepidine or quinoline having been formed. The investigation of the oil is continued.

In another paper (p. 282) the author states that by the action of caustic alkalis on cinchonidine, quinoline, lepidine, and a dextrorotatory viscous oil are formed. From quinine and quinidine he has obtained an amorphous optically active substance and two optically inactive bases, one of which is easily converted into a hydrate melting at 52°.

A. T.

Decomposition of Cinchonine by Sodium Ethoxide. By A. Michael (*Amer. Chem. J.*, **7**, 182—188).—The best results were obtained by heating 6 grams of caustic soda, 6 grams of cinchonine, and 60 c.c. of absolute alcohol at 130—135° for 8—10 hours; no gaseous products were formed. The contents of the tubes were freed from alcohol, a large quantity of water added, and the whole extracted with ether. The ethereal extract when evaporated and distilled with steam yielded a very small quantity of volatile bases, about 1 per cent. of the cinchonine employed. The bases not volatilised by steam amounted to over 80 per cent. of the cinchonine employed; they could not be separated by distillation, but fractional precipitation

with platinum chloride showed that the material was almost perfectly homogeneous. The free base, $C_{20}H_{26}N_2$, is a heavy, reddish-yellow, viscous oil; the salts are, so far as examined, amorphous, except the platinochloride, $C_{20}H_{26}N_2,H_2PtCl_6$. The aqueous alkaline solution, left after extraction with ether, contains formic acid. The reaction is therefore probably expressed by the equation $C_{19}H_{22}N_2O + EtONa = C_{18}H_{21}N_2Et + H{\cdot}COONa$; whence cinchonine would be an amide of the base $C_{18}H_{22}N_2$, and of formic acid; the volatile bases obtained by other experimenters, are decomposition products of the base here described. H. B.

Artificial Preparation of Cocaine and its Homologues. By W. Merck (*Ber.*, **18**, 2952—2955; compare Abstr., 1885, 1249).—Cocaine can be prepared by heating anhydrous ecgonine with benzoic anhydride and methyl iodide for 10 hours at 100°; the product is poured into water, purified by extraction with ether and filtration through animal charcoal, and the base is liberated by means of sodium carbonate; the yield is small.

Cocethyline, $C_{18}H_{23}NO_4$, is prepared by heating benzoylecgonine with ethyl iodide and alcohol for eight hours at 100°. It crystallises from alcohol in splendid prisms with vitreous lustre, melting at 108—109°. The *platinochloride* forms bright yellow rhombic plates; it resembles cocaine platinochloride, but is more crystalline. Like cocaine, the base is an anæsthetic. N. H. M.

Lupanine, an Alkaloïd from the Seed of the Blue Lupine. By M. Hagen (*Annalen*, **230**, 367—384).—The seeds of the blue lupine, *Lupinus angustifolius*, contain a liquid alkaloïd, *lupanine*, $C_{15}H_{25}N_2O$, but do not contain either of the alkaloïds lupinine,

$$C_{21}H_{40}N_2O_2,$$

or lupinidine, $C_8H_{15}N$, which Baumert (Abstr., 1881, 831; 1882, 229, 873; 1883, 100, 224) found in *Lupinus luteus*. The alkaloïd is extracted from the seed by Liebscher's process (*Ber. landw. Institut zu Halle*, Heft II).

Lupanine is a thick, non-crystallisable syrup, possessing a bitter taste and a strongly alkaline reaction. It has a pale-yellow colour, and exhibits a green fluorescence. Lupanine attacks the skin, and fumes in the presence of hydrochloric acid. It is precipitated from its salts by soda and potash, but liberates ammonia from its compounds. The alkaloïd is sparingly soluble in water and alcohol, but is freely soluble in ether, chloroform, and light petroleum. The liquid does not boil at 290° under a pressure of 130 mm. The *hydriodide*, $C_{15}H_{25}N_2O,HI + 1\frac{3}{4}H_2O$, forms large, monoclinic crystals, which are sparingly soluble in water and alcohol. The *hydrochloride*, $C_{15}H_{25}N_2O,HCl + 2H_2O$, appears to crystallise in the quadratic system. It is a hygroscopic salt, soluble in water and alcohol, but insoluble in ether; it melts at 127°.

The *thiocyanate*, $C_{15}H_{25}N_2O,HSCN + \frac{1}{2}H_2O$, forms transparent crystals, soluble in hot alcohol. The sulphate and oxalate do not crystallise. The *platinochloride*, $C_{15}H_{25}N_2O,H_2PtCl_6 + 3\frac{1}{2}H_2O$, is not

distinctly crystalline; it is sparingly soluble in cold water and cold alcohol, and is insoluble in ether. The *aurochloride* forms silky, golden needles, insoluble in water, alcohol, and ether.

Lupanine unites with methyl iodide to form the methiodide,

$$C_{15}H_{25}N_2O,MeI,$$

which is decomposed by moist oxide of silver, yielding the hydroxide, $C_{15}H_{25}N_2O,MeOH$. This base exists as a colourless syrup. It unites with acids, forming a series of crystalline salts. Like lupanine, it forms an acid platinochloride, $C_{15}H_{25}N_2O,MeHPtCl_6 + H_2O$. The *aurochloride* forms triclinic needle-shaped crystals, soluble in hot water. W. C. W.

Alkaloïds in Old Flour. By Balland (*J. Pharm.* [5], **11**, 341—342).—Flour kept in sacks for some time, shows traces of the presence of alkaloïds, and later the quantity formed becomes more and more appreciable. The flour is extracted with ether; the solution thus obtained gives on evaporation a fatty residue which is acid, especially in the case of very old flour; its odour is disagreeable and penetrating, and its taste is very acrid. The presence of alkaloïds in an aqueous extract of the residue can readily be detected by means of suitable reagents. Flour 12 to 18 months old gives sensible amounts. The extract administered to sparrows kills them after several hours, whilst fresh flour gives no such results. J. T.

New Method of Separating Globulins from Albumins. By V. Michailoff (*J. Russ. Chem. Soc.*, 1885, 348—354).—In a former communication (Abstr., 1885, 69) a method of preparing pure albumin was described, which consists in precipitating filtered white of egg with ammonium sulphate and dialysing the precipitated albuminoïd matter, after dissolving it in water. The present paper is a description of the separation of the different albuminoïd bodies contained in the serum of blood. A convenient volume of serum (20—50 c.c.) is saturated with solid ammonium sulphate until the whole of the albuminoïd matter is precipitated. The precipitate is thoroughly washed with saturated ammonium sulphate solution, to free it from other mineral salts, dissolved in the smallest possible volume of water, and placed in a dialyser. After 2—3 days' dialysing, water is added to the solution, which is then filtered. The whole of the globulins remain on the filter, whilst the albumin passes into the filtrate. On saturating this with magnesium sulphate at 30°, not the slightest precipitate is formed. The author considers that globulin and albumin originally form a complex group in the serum, which, after elimination of the mineral salts, is split up by the action of an excess of water. It is noticed that on concentrating the dialysed mixture of serum, globulin, and albumin at low temperatures (70—75°), the globulin precipitate disappears as soon as a certain degree of concentration is reached. The existence of a compound of albumin and globulin in the serum is the more probable, as the reaction of albumin is acid (*loc. cit.*). As regards the globulins, or at least substances closely related to them, some data established by Danilevsky

(*Centr. Med. Wiss.*, 1880, 51) seem to point to their alkaline character. A. T.

The Hæmoglobin Molecule. By O. Zinoffsky (*Zeit. physiol. Chem.*, **10**, 16—34).—Former analyses of hæmoglobin have shown that the molecule contains at least 600 atoms of carbon. This is a minimal number reckoned on the basis that only one atom of iron is present. Sulphur is also a constituent of hæmoglobin, but previous determinations of the amount present show very contradictory results: hence the supposition first advanced by Lehmann, that the crystallised substance hæmoglobin is not a chemical unit, but consists of hæmatin, which contains iron, mechanically mixed with a crystallised proteid. A seeming confirmation of this theory has been recently advanced by Struve (*Zeit. pract. Chem.*, 1884), who found that by means of alcoholic ammonia, hæmatin could be extracted from the crystals, leaving them colourless. The author, however, shows that the conflicting results as to the quantity of sulphur present are due to bad methods of preparation of hæmoglobin, and that hæmoglobin is, after all, a chemical unit.

The method of preparation is as follows:—The red corpuscles are collected from defibrinated horse's blood, mixed with three times their volume of distilled water, the mixture warmed to 35°, and the hæmoglobin thus dissolved. The colourless stromata of the corpuscles float in the liquid, but are too small to be separated by filtration. They are, therefore, dissolved by adding a small quantity of ammonia or ether. If ammonia is used, it must be afterwards neutralised by dilute hydrochloric acid. Crystallisation of the hæmoglobin is brought about by the addition to the liquid of a quarter of its volume of alcohol, the mixture being kept at 0° for 48 hours. The crystals form abundantly, are filtered off, washed with 75 per cent. alcohol at 0°, redissolved in water at 35°, and purified by repeated recrystallisation. By this method three preparations of pure hæmoglobin were made and submitted to analysis, and the ratio of iron to sulphur atoms found to be as 1 : 2. The formula deduced for hæmoglobin is $C_{712}H_{1130}N_{214}S_2FeO_{245}$. The author further considers that as decomposition-products of hæmoglobin, one molecule of hæmatin with 34 atoms of carbon, and two molecules of proteïd (globulin), each with one atom of sulphur and 339 of carbon, are formed. He, however, thinks it probable that each molecule of proteïd contains four atoms of sulphur and 1356 of carbon (that is, granting that peptones are decomposition-products of proteïd, and that each molecule of peptone probably contains two atoms of sulphur united in different ways). W. D. H.

Action of Ammonia on Hæmin. By M. Shalféeff (*J. Russ. Chem. Soc.*, 1885, 203—204).—Hæmin crystals, when treated with an alcoholic solution of ammonia, become colourless, without losing their crystalline form or undergoing any change in volume; the ammoniacal solution deposits brown, translucent, globular aggregates of needles. These crystals show double refraction in a higher degree than hæmin crystals, whilst the colourless crystals have en-

tirely lost this property. The author terms the colourless constituent of hæmin, hæminostromine, the colouring matter, hæminic acid.

A. T.

On Mucin obtained from Tendons of the Ox. By W. F. Loebisch (*Zeit. physiol. Chem.*, **10**, 40—79).—The most important recent work on mucin is that of Landwehr (*ibid.*, **6**, **7**, **8**, **9**). Previously it was known that mucin was an albuminoïd, soluble in dilute alkalis, precipitable by acetic acid, and that after heating with dilute sulphuric acid, a reducing substance of unknown nature is formed. The author holds that a proteïd and a carbohydrate are the products of decomposition of mucin, and that mucin is not merely a mechanical mixture of two such substances, as Landwehr supposes, but probably a glucoside. He prepares mucin by precipitating a lime-water extract of the tendons with acetic acid. After 24 hours, the length of time the lime-water and the tendons are in contact does not cause more mucin to be dissolved, nor does the temperature of the lime-water make any difference. Boiling causes mucin to be no longer precipitable by acetic acid; 1 to 5 per cent. acetic acid is the best strength of acid to use, weaker acid causing only a cloudiness, not a precipitate. Unlike Landwehr's mucin (from saliva and snails), tendon-mucin is not changed into coagulated proteïd by boiling or by remaining under alcohol.

The amount of mucin may be estimated not only by weighing the dried acetic acid precipitate, but by the decrease of alkalinity of an alkaline solution employed to dissolve it, mucin having an acid reaction. The author's formula for mucin is $C_{160}H_{256}N_{32}SO_{80}$. By heating with dilute sulphuric acid, it yields a carbohydrate of the formula $C_{12}H_{20}O_{10}$; by still further heating, a reducing sugar, $C_6H_{12}O_6$, is obtained; this differs from Landwehr's "animal gum" in forming a clear solution with water; a proteïd is also formed. W. D. H.

Physiological Chemistry.

Occurrence of Peptone in Hen's Eggs during Incubation. By W. Fischel (*Zeit. physiol. Chem.*, **10**, 11—13).—The author had observed that the occurrence of peptone in the urine of puerperal women is a constant physiological phenomenon. He accounted for this (*Archiv. Gynäk.*, **24**, 425) by supposing that peptones are formed in the tissues of the embryo during development, that excess of this diffuses into the maternal blood, and thence appears in the urine. Confirmation of this theory was obtained by examining the embryonic tissues and yolk of developing eggs. In all, 42 specimens were examined, the period of incubation varying from the second to the nineteenth day. In eight cases, peptones were found both in the embryonic tissues and in the yolk, in one embryo as much as 54 mrgms. being present. Peptones were never found before the fifteenth day, and in some cases not even after that date. The author hopes to

continue his investigation of the subject with a larger supply of material. W. D. H.

Occurrence of Peptones in Fibromata of the Uterus. By W. Fischel (*Zeit. physiol. Chem.*, **10**, 14—15).—Although peptone is not a normal constituent of the uterus, yet it occurs in those overgrowths of the uterine muscular walls known as fibromata or myomata. On examining one of these tumours, abundant evidence of peptones was found in the watery extract after the precipitation of the other proteids. This would seem to be contained in the tumour itself, not in the contents of its blood-vessels and lymphatics, which were abundant, because in a similar tumour, the blood and lymph were examined and peptones shown to be absent, although it was present in the muscular tissue of this tumour, as in the one first described.

W. D. H.

Relations of the Phosphates in Urine. By A. Ott (*Zeit. physiol. Chem.*, **10**, 1—10).—The acid reaction of urine is now known to be due to an excess of acid over normal phosphates. The author gives a series of analyses showing the relative quantities of phosphoric acid present in the urine combined in the form of acid and normal phosphates. Huppert's method of analysis was used. The urine was collected daily at 10 P.M., 8 A.M., and 2 P.M. Meals were taken after each collection of urine; dinner and supper consisting of meat and vegetables, breakfast of coffee and bread. The average of the analyses shows that the ratio of P_2O_5 combined as normal phosphate to that combined as acid phosphate was as follows:—Evening urine (2 P.M. to 10 P.M.) as 91 : 100, night urine (10 P.M. to 8 A.M.) 56 : 100, morning urine (8 A.M. to 2 P.M.) 58 : 100, or for the total urine for 24 hours as 69 : 100.

The large amount of normal phosphates present in the evening's urine illustrates the previously known fact of the relation between the food taken and the phosphates in the urine.

Erlenmeyer (*Ber.*, **9**, 1839) has shown that acid calcium phosphate is soluble in 700 parts of water. But that the urine is able to hold more than this in solution is accounted for by the presence of other salts in it, for it is known that if acid calcium phosphate and calcium chloride be mixed in equivalent quantities, a solution can be obtained in which the phosphate is dissolved in only 34·2 parts of water. Similarly it is shown that the normal phosphate is more soluble in urine than in water, salts such as potassium phosphate and sodium chloride aiding its solution.

By heating the aqueous solution of both phosphates, they are precipitated, the acid phosphate being changed into the normal phosphate, whilst phosphoric acid passes into solution. But in normal urine no such precipitate, or only a very slight one occurs. This is accounted for again by the presence of other salts, especially magnesium phosphate, potassium phosphate, and sodium phosphate. This can be shown experimentally with the individual salts, and normal urine contains such proportions of these salts as to prevent precipitation by heat. W. D. H.

Composition of the Milk of Shorthorns and other Cows and Goats. By P. Vieth (*Bied. Centr.*, 1885, 603—606).—The following results were obtained by Völcker in 1881—84, when examining the milk of several cows :—

Shorthorns.

	Lactation.	Daily yield.	Sp. gr.	Dry matter.	Fat.	Cream in creamometers.
	weeks.	kilos.		per cent.	per cent.	per cent.
Minimum ...	1	4·990	1·0270	10·9	2·3	3
Maximum ...	31	25·473	1·0360	15·1	6·6	16
Average	10	17·663	1·0315	12·6	3·7	9
Jerseys.						
Minimum ...	—	8·051	1·0300	12·3	3·0	7
Maximum ...	23	18·377	1·0370	14·8	5·6	20
Average	8	13·851	1·0327	13·5	4·1	12
Guernseys.						
Minimum ...	2	8·392	1·0300	12·1	2·5	8
Maximum ..	28	16·103	1·0340	15·2	6·3	19
Average.....	15	11·244	1·0319	13·9	4·6	13
Ayrshires.						
Minimum ...	—	11·340	1·0288	11·6	2·6	2
Maximum ...	74	21·880	1·0360	14·9	5·6	17
Average	14	16·183	1·0324	13·5	4·2	11
Dutch.						
Minimum ...	2	16·556	1·0316	9·9	1·9	6
Maximum ..	12	27·329	1·0360	14·2	4·4	14
Average	6	21·793	1·0330	12·0	3·1	9
Goats.						
Average	16	1·767	1·0329	14·1	4·9	—

The author has during three years examined the milk of 300 shorthorns, and finds the following yearly average :—

	1881.	1882.	1883.
Specific gravity	1·0326	1·0330	1·0328
Dry matter, per cent.	13·0	13·1	13·0
Fat, per cent.	3·8	3·8	3·7

E. W. P.

Hypnotic Properties of Phenyl Methyl Ketone. By D. Beaumetz and G. Bardet (*Compt. rend.*, **101**, 960—961).—Phenyl methyl ketone has powerful hypnotic properties, and in this respect surpasses chloral and paraldehyde. When administered together with a little glycerol in gelatin capsules, in doses of 0·05 to 0·15 gram, it produces profound sleep, followed by no evil after-effects, except that the breath is disagreeable in consequence of the elimination of the ketone by the lungs.

If the ketone is injected under the skin of the guinea-pig in doses of 0·5 to 1 gram, it produces a remarkable hypnotic torpor, and this gradually passes into a state of coma which ends in death in five or six hours. C. H. B.

Poisonous Product of the Culture of Comma Bacillus. By W. Nicati and Rietsch (*J. Pharm.* [5], **11**, 292—296).—The authors have already shown the poisonous effect of comma bacillus cultures when injected into the veins of dogs (Abstr., 1885, 180). In the present paper they show that a product obtained by Stas' method from these cultures is also poisonous. As contradictory or negative results have been previously published, the authors seek to ascertain if this poison is constantly or only accidentally formed. J. T.

Chemistry of Vegetable Physiology and Agriculture.

Composition and Fermentation of Invert Sugar. By E. Bourquelot (*Compt. rend.*, **101**, 958—960).—A reply to Maumené and to Leplay. The author shows that Leplay's results really support his own conclusions. C. H. B.

Inverting Ferment of Cane-sugar. By A. Ladureau (*Ann. Agronom.*, **11**, 404—408).—Certain saccharometer tubes containing solutions of cane-sugar to be examined optically, were found to gradually lose their rotatory power on being allowed to remain for some hours. At the end of two or three days the whole of the cane-sugar was found to be converted into invert sugar. Subacetate of lead, far from hindering this inversion, appears to favour it. The ferment appeared to be attached to the tubes used, for when these were washed with hydrochloric acid, phenol, or salicylic acid, no inversion occurred.

Neither did it occur in solutions of sugar kept in glass vessels. The author explains by means of this fact the otherwise unaccountable deterioration of the sugar (accompanied by inversion) which occurred in a sugar refinery under his own observation. J. M. H. M.

Zymotic Properties of Certain Virus. By S. Arloing (*Compt. rend.*, **101**, 819—821).—*Bacillus anthrax* and *Micrococcus septicus puerperalis* from an old cultivation, produce no distinct fermentation, but *M. septicus puerperalis* from recent cultivations, and especially the anaërobic virus of gangrenous septicemia, and emphysematous anthrax in beef, cause rapid fermentations in solutions of glucose, lactose, saccharose, and mannitol, and act even still more energetically on solutions of starch, dextrin, and inulin. Hydrogen and carbonic anhydride are evolved in varying proportions, and the solutions, which become more or less acid, contain glucose. The deposits formed during fermentation are capable of producing the same change in fresh solutions.

The recently dried virus from septicemia and anthrax produce similar results, but if they have been dry for a long time, or if their pathogenic activity has been lessened by the action of heat, they lose their zymotic action without losing their injurious properties. It would seem, therefore, that the pathogenic properties of these micro-organisms are partially distinct from their zymotic properties; the latter disappear first, and seem to reside in the mycelium itself, and not in the spores.

The analogy between virulent micro-organisms and ferments can no longer be doubted. C. H. B.

Intramolecular Respiration. By Pfeffer (*Ann. Agronom.*, **11**, 426—432).—Some experimentally observed values of the ratio between intramolecular and normal respiration $\left(\frac{I}{N}\right)$ are as follows:—Bean, 0·994, 1·094, 0·829, 1·197; wheat, 0·490; white mustard, 0·177, 0·181; turnip, 0·249; hemp, 0·339; sunflower, 0·354; lupine, 0·244—all the foregoing ratios refer to the young plants. In the fruits of *Heracleum*, before maturity, the ratio was 0·416; young branch of *Abies excelsa*, 0·077; flowering stem of *Orobanche ramosa*, 0·321; spadix of *Arum maculatum*, 0·615; branch of *Ligustrum vulgare*, 0·816; *Lactarius piperatus*, 0·316; *Hydnum repandum*, 0·256; *Cantharellus cibarius*, 0·666; beer yeast cultivated with milk-sugar, 0·310. The remainder of the paper is devoted to a discussion of the theories which have been advanced as to the nature of normal and intramolecular respiration, and their relations to each other. Pfeffer holds provisionally that the same cause produces intramolecular or normal respiration according as the plant is or is not deprived of oxygen.

J. M. H. M.

Respiration of Leaves in the Dark. By Deherain and Maquenne (*Compt. rend.*, **101**, 887—889).—These experiments were undertaken with a view to establish the authors' previous conclusion (Abstr., 1885, 927) that leaves retain part of the carbonic anhydride which they produce, and that consequently an analysis of the air

surrounding the leaves gives no accurate information regarding the ratio between the oxygen absorbed and the carbonic anhydride produced. A known quantity of the leaves of *Euonymus japonica* was placed in a known volume of pure air, and after some time the air surrounding the leaves was analysed, and then by making the vacuum complete, the air retained by the leaves was also extracted, and the second quantity of gas analysed. The first result gives the *apparent ratio* $CO_2 : O$; the second and first together give the *real ratio*. The difference between the two values depends on the ratio of the volume of the leaves to the volume of the space in which they are confined, and if the leaves occupy more than one-tenth of the space, the difference becomes considerable.

The authors also find that if the leaves are placed in an atmosphere of carbonic anhydride in the dark, they rapidly absorb a considerable quantity of this gas. C. H. B.

Germinative Power of Seeds after Exclusion of Air and Drying at High Temperatures. By Wilhelm (*Bied. Centr.*, 1885, 611—613).—When seeds were dried at 50—60° and kept in hermetically sealed vessels, it was thought that they retained their germinative power most effectively. The author has carried on his experiments in the same direction on the same sample of seed for six years. For the sake of comparison, some seed was kept in bags, so as to preserve it from dust; another sample was hermetically sealed up, and both samples exposed to the ordinary temperature; two other samples were exposed for two hours, the one to a temperature of 50°, the other to 75°. The seeds were winter wheat, rye, oats, and linseed. The results: exclusion from the air enables the seed to retain its germinative power longer than when air has free access to it; this is especially the case with rye. Two hours' heating to 50°, whereby some water is removed, is very effective for the preservation of the seed. After exposure to higher temperatures than 50°, seeds, at least the cereals, germinate more slowly than if only exposed to a lower temperature. Seeds which have been artificially dried, when subsequently moistened, absorb more water than they would otherwise have done; and old seeds, as a rule, germinate more slowly than new seeds, especially if they have been exposed to the air.

E. W. P.

Absorption of the Non-alimentary Substances by Plants. By Knop (*Ann. Agronom.*, **11**, 418—419; from *Bot. Centr.*, **22**, 35).—Maize plants were grown in nutrient solutions containing 2 grams per litre of the following mixture of salts:—4 parts calcium nitrate, 1 part potassium nitrate, 1 part potassium phosphate, and 2 parts crystallised magnesium sulphate. One solution was neutral, the other was acidified by the addition of 0·07455 gram free phosphoric acid.

The phosphates of most metals are soluble in the acid solution, and were added to it in a freshly precipitated state, mixed with phosphate of iron. The author's previous researches have shown that iodine and bromine, in small quantities, are not more injurious than chlorine, but that in larger doses iodine is the most injurious,

then bromine, and chlorine least. Also that zinc, boric acid, cobalt, copper, silver phosphate, and gold chloride are poisonous; but strontium, barium, and manganese are absorbed without injury. The researches reported in the present paper gave the following results: Ammonium vanadate (50 mgrms. per litre) is poisonous at the end of two days. Roots coloured white by the lower oxides of vanadium soon cease to grow, but as soon as all the salt is absorbed the plants become healthy again. Molybdic acid acts in the same way. Phosphotungstic acid in doses of 0·05—0·1 gram is very poisonous. Tellurous acid, being scarcely soluble in the nutrient solution, is not absorbed. Telluric acid (0·05—0·1 gram per litre) is without action; whilst selenious and selenic acids are very poisonous. Arsenious acid is very poisonous, but potassium arsenate given in 0·05 gram dose to plants of maize with 10 to 15 leaves, did not hinder normal growth and fructification, nor kill a *Volvox globator* or a mould. Cadmium and thallium are poisonous. Lead phosphate feebly retarded the general development of the plant without disorganising the various functions. Bismuth resembles lead in this respect. Oxalic, humic, malic, tartaric, citric, benzoic, and succinic acids are without influence when very dilute. Potassium ferrocyanide rapidly remedies chlorosis; in 0·1 gram dose it simply arrests the growth of the plant, which nevertheless remains green and healthy until autumn. Hydroxylamine hydrochloride, in the proportion of 0·5 gram per litre, is very poisonous; so are mellitic acid and ammonium mellitate in doses of 1 gram. It is doubtful whether nickel and bismuth are absorbed, since they cannot be found in the plant. Chromium and uranium oxides are not absorbed because of their insolubility. The following substances act fatally on the roots, whether or not they are really absorbed: silver oxide, gold chloride, platinum chloride, vanadic, molybdic, and phosphotungstic acids, thallium oxide, selenious and selenic acids, boric and chromic acids. J. M. H. M.

Ash of the Pollen of Pinus Silvestris. By A. Famintzin and S. Przibytek (*J. Russ. Chem. Soc.*, 1885, 371—372).—On drying the pollen of *Pinus silvestris* at 100—105° it loses 6·79 per cent. in weight; the dried substance gives 3·30 per cent. of ash containing—

K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3, Al_2O_3.	MnO.	P_2O_5.	SO_3.	Cl.
35·25	3·62	0·88	7·00	5·30	trace	29·86	14·83	0·99

nitrogen by Kjeldahl's method = 2·40 per cent.; if the whole of this nitrogen be calculated in the form of albuminoïd matter (which obviously is only approximately correct), the quantity of the latter in the pollen is 15 per cent. (compare Von Planta, this vol., p. 91).

A. T.

Glycyrrhizin in Myrrhis Odorata. By Schroeder (*Arch. Pharm.* [3], **23**, 621—622).—Guignet has remarked the presence of glycyrrhizin in plants not belonging to the Papilionaceæ; this induced the author to examine *Myrrhis odorata* both by Robiquet's method and that of Guignet. The latter (treatment with acetic acid, then with alcohol, and after concentration, separation by means of

water, &c.) gave unsatisfactory results. The plant was treated with aqueous ammonia, sulphuric acid added to the filtrate, the precipitate evaporated to dryness with barium carbonate, treated with alcohol, and the filtrate evaporated. Repeated attempts were made to obtain a crystallised product, but without success. The reactions of glycyrrhizin were obtained. J. T.

Nitrogenous Constituents of Pumpkin Sprouts. By E. Schulze (*J. pr. Chem.* [2], **32**, 433—461).—In continuation of his work on this subject (compare Abstr., 1880, 180), the author describes in full detail the methods by which he isolated or recognised the following substances:—Glutamine, asparagine, tyrosine, leucine, vernine, members of the xanthine-group (probably as decomposition products of nucleïn), ammonium salts, and nitrates. Most of these substances occur in both axial organs and cotyledons; but asparagine and vernine were found only in the cotyledons, glutamine in the axial organs only. A. J. G.

Root of Danais Fragrans. By E. Heckel and F. Schlagdenhauffen (*Compt. rend.*, **101**, 955—957).—This root, contrary to the statement of Bourdon, contains no alkaloïd. The colouring principle, which is also the therapeutic agent, was isolated by precipitating the extract of the root with basic lead acetate, decomposing the precipitate with hydrogen sulphide, and evaporating the red solution to dryness after filtering. The residue is a greenish-brown substance, completely soluble in alcohol, acetone, and methyl alcohol, less soluble in chloroform and ether, and only slightly soluble in cold water, but completely soluble in boiling water. The greater part sublimes unchanged when heated, but a small portion is carbonised. This substance, to which the author gives the name *danaïn*, has the composition $C_{14}H_{14}O_5$, and splits up into half its own weight of glucose, and a resinous amorphous compound, *danaïdin*, which probably has the composition $C_{22}H_{20}O_6$. C. H. B.

Composition of Spurrey (Spergula Arvensis), Spurrey Seed, and Spurrey Silage. By J. M. H. Munro (*Field*, 1885, 386—387).—Spurrey, recently recommended as a suitable crop for growing on barren sands with a view to ensiling, has the following composition, the specimen analysed being cut on June 12th, partly in flower and partly in seed. Water, 81·43; dry substance, 18·57. The air-dried spurrey, or hay, contained in 100 parts:—Water, 10·79; insoluble ash, 5·33; soluble ash, 4·77; crude fibre, 23·82; oil (light petroleum extract), 3·80; resin, &c., soluble in ether, 1·47; true albuminoïds, 8·75; starch, digestible fibre, amides, &c., 41·22. The total nitrogen was 1·82 per cent., and the albuminoïd nitrogen 1·40 per cent; 77 per cent. of the total nitrogen was thus albuminoïd. Silage was made on a small scale (in a glass vessel) from a portion of the same sample, and its analysis, compared with that of the fresh herbage, is exhibited in the following tables:—

	Fresh herbage.	Fresh silage.	Percentage composition of dry substance of	
			Herbage.	Silage.
Water	81·43	77·23	—	—
Ash, insoluble in water	1·12	0·88	6·03	3·86
Ash, soluble in water	0·99	0·98	5·34	4·30
Crude fibre	4·96	5·75	26·70	25·25
Ether extract	1·09	1·78	5·90	7·82
Albuminoïds	1·82	0·76	9·81	3·34
Volatile acid, reckoned as acetic	—	0·06	—	0·26
Fixed acid reckoned as lactic	—	0·94	—	4·13
Starch, digestible fibre, soluble carbohydrates,* amides, and other non-albuminoïd nitrogenous substances	8·59	11·62	46·22	51·04
	100·00	100·00	100·00	100·00
Total nitrogen	0·378	0·384	2·04	1·68
Albuminoïd nitrogen	0·291	0·122	1·57	0·54
*Non-albuminoïd nitrogen	—	0·262	0·47	1·14
Nitrogen soluble in water	0·087	0·289	—	1·27

The loss of mineral matter is apparent only, and is caused by adventitious sand in the samples. The crude fibre and the fat appear to undergo no alteration. Two-thirds of the albuminoïds are lost during the fermentation in the silo; some of their nitrogen is absolutely lost (as nitrogen gas), but most of it exists in the silage as ammonia, amides, &c. As bearing on this point, an experiment made in 1883 on the fermentation of the nitrogen of gelatin, first with ammonia, and afterwards with nitric acid, under the influence of soil-ferments, is recorded in this paper. The total loss of weight suffered by the spurrey during its conversion into ensilage did not exceed 8·4 per cent. of the dry substance. The starch contained in the seeds of the spurrey herbage was found unaltered in the fresh silage, but the sour silage could not be dried in a steam oven without total conversion of this starch into carbohydrates, giving no iodine reaction. A slight loss of nitrogen, and of non-nitrogenous matter, a considerable transformation of albuminoïds into less valuable substances, and a development of free acid at the expense of a little sugary or starchy material, probably sum up all the important changes brought about in the manufacture of good silage. Some specimens of silage will keep well on exposure to the air, others become mouldy, others rapidly putrefy: the causes of the differences are at present unknown, but probably depend on the proportions of water and free acid. The lower layers of silage contains more, the upper layers less water than the original herbage.

Spurrey seed contains in 100 parts:—Water, 11·48; ash, 2·58;

crude fibre, 13·93; oil (light petroleum extract), 8·52; resin, soluble in ether, insoluble in alcohol, 2·24; other substances extracted by ether, 1·44; albuminoïds, 10·13; starch, digestible fibre, &c., 49·68. The nitrogen is almost entirely albuminoïd, and amounts to 1·62 per cent.

The black testa of the seed contains a substance with a peacock-blue fluorescence, similar to the *peonio-fluorescin* discovered by Dragendorff in the testa of peony seeds. This substance is insoluble in water and light petroleum, soluble in ether and alcohol. To extract it, the crushed seeds are exhausted first with light petroleum to free them from oil, and then with alcohol. The alcoholic solution is evaporated to dryness, and the residue boiled with water (which dissolves out tannin and other substances amounting to 5 per cent. of the seed). The residue insoluble in water is an olive-green powder, whose alcoholic or ethereal solution exhibits fluorescence of increased brilliancy, but this fluorescence disappears after some days, the solutions becoming dark-brown. This solution gives a peculiar taste and odour to spurrey seed. J. M. H. M.

Absorption of Free Nitrogen from the Atmosphere by Argillaceous Soils. By Berthelot (*Compt. rend.*, **101**, 775—784). —Four different kinds of soil, namely, two samples of yellow argillaceous sand, white clay, and crude kaolin were placed in open cylindrical pots of glazed earthenware and left for many months in a closed apartment, freshly plastered, well lighted, dry, and free from any effluvia. Samples for analysis were taken from the various pots at intervals. In all four cases, the amount of combined nitrogen increased continually and very considerably, whilst nitrification remained stationary, and the proportion of ammonia, always small, was either constant or tended to decrease.

The same soils were placed in glazed porcelain pots perforated at the bottom, and the pots were supported on a table in a meadow at a height of 0·7 m. from the ground. The pots were protected from vertical rain by a roof, whilst the air could circulate freely round them, and they were exposed to the action of oblique rain. During the latter part of the experiment, the soils were watered with distilled water on account of the extreme dryness of the weather. A similar series of pots was exposed, without any protection from the weather, on the top of a tower 29 m. above the soil of a meadow. In both series the result was the same as in the first series; the amount of combined nitrogen continually increased. The amount of nitrogen in the rain which fell during the latter experiments was estimated by collecting the rain in a hygrometer with a known collecting surface and determining the amount of ammonia. The atmospheric ammonia was estimated by placing a vessel containing dilute acid by the side of the pots containing the soils. The amount of nitrogen derived from nitrogen compounds in the atmosphere was much less than the amount of nitrogen absorbed by the soils, and it follows from this result that the absorption of nitrogen by these soils is independent of the combined nitrogen in the air, or, in other words, free nitrogen is absorbed.

In a fourth series of experiments, 1 kilo. of each soil was placed in a flask of 4 litres capacity, moistened with water, and the flasks stoppered and placed in diffused light or in the dark, as the case might be. In all the soils employed, the amount of combined nitrogen continually increased, the absorption taking place somewhat more rapidly in the light than in the dark. The amounts of nitrates and ammonia remained constant or diminished.

It was found, however, that if the soils were sterilised by heating at 100° for two hours, and only filtered air was allowed to enter the flasks, or even if the sterilised soil was freely exposed in a closed apartment, no increase in the amount of nitrogen was observed.

From these results it follows that argillaceous soils have the power of absorbing free nitrogen from the air, the absorption taking place under the influence of living organisms. This absorption is perfectly distinct from nitrification. It does not take place in winter, but proceeds most rapidly when vegetation is most active.

The following table gives the amount of nitrogen absorbed by 1 kilo. of the different soils during six months; that is, from April to October, 1885 :—

	Initial nitrogen.	Closed room.	Meadow.	Tower.	Closed flask in the light.
Yellow argillaceous sand, I.	0·0910	0·1179	0·0983	—	0·1289
" " " II.	0·1119	0·1639	0·1295	0·1396	0·1503
White clay	0·0210	0·0407	0·0353	0·0557	0·0494
Crude kaolin	0·1065	—	0·1144	0·1497	0·1236

The absolute weight of nitrogen absorbed was 0·02—0·04 gram per kilo., or, calculating from the surface exposed in the pots, 26—32 kilos. per hectare. This last number is, however, too low, since absorption is not confined to the surface, but extends to a considerable depth.

C. H. B.

Changes occurring during and the Action of Water in Irrigation. By J. König and C. Böhmer (*Bied. Centr.*, 1885, 577—594).—The researches, of which mention was made (Abstr., 1882, 655), have been continued in the South of France on fields cultivated under a six-course system. It was found that with the same absolute amount of water flowing, the evaporation from equal surfaces was the same. Water, when present in small quantities, was more thoroughly exhausted of its constituents than when much was present; that is, the absolute quantity of materials removed by like surfaces was in all cases alike. Poor soils abstract more mineral matter from water than rich; consequently, water cannot be so frequently used on poor as on fertile land. The manuring action, or the cession of minerals to the soil, is not absolutely dependent on the absorptive capacity of the soil, but the plants themselves absorb a considerable part, the quantity varying with their energy of growth. This manuring action is by no means the chief advantage which the soil gains, for

the water removes some useless material and reduces the acidity in its passage through. The quantity of manure which water brings can be easily replaced by artificial manures, but the neutralisation of the acid must be accomplished by ploughing, &c. The last result is accomplished by irrigating according to Vincent's system (simple surface or gravitation), but this requires plenty of water and natural subsoil drainage, by which at least 100 litres per hectare a second can flow away. If the supply of water is wanting, when only 10·70 litres are available, then the oxidising action must be assisted by drainage; in such a case Petersen's valvular drainage system may be employed with great advantage. With plenty of fall, with 20—30 litres at disposal, Abel's system is best. E. W. P.

Effect of Various Manures on the Ash of Tobacco. By W. H. Jordan (*Bied. Centr.*, 1885, 598—600).—In order that tobacco, when prepared for smoking purposes, shall burn well, it must contain but little chlorides; consequently, all manures containing chlorides must be carefully avoided. Tobacco also requires much potash; therefore, the sulphate and carbonate (potashes) should be employed. The analyses show that the absolute quantity of ash is not much altered, but that the constituents of that ash vary very considerably according to the manure. E. W. P.

Analysis of Tobacco Leaves and Stems. By E. H. Jenkins (*Bied. Centr.*, 1885, 623—627).—The results stated in this article are similar to those in the previous Abstract. There appears to be no relationship between the capability for burning and the percentage of potassium carbonate in the plant. E. W. P.

Valuation of Unexhausted Manures. By Sir J. B. Lawes and J. H. Gilbert (*Jour. Roy. Agri. Soc. Eng.*, **42** (1885) [2], 590—611).—The authors revise the table, originally issued 25 years ago, containing their estimates of the manurial value of one ton of various farm foods, after deducting that portion of the manurial constituents of each food which may be supposed, in the case of a fattening animal, to appear as increase of live-weight. The calculations are made on the same principles as the former ones, and the alterations are due in some measure to the adoption of average percentage compositions based on more recent analyses, but chiefly to the alteration in the price of ammonia, which is now valued at 6*d.* per lb. instead of 8*d.*; phosphoric acid and potash are now valued at 3*d.* and 2½*d.* per lb. as against 2¼*d.* and 2*d.* per lb. respectively. Whereas in the former table the manurial value of a ton of linseed cake consumed by a fattening animal appeared as £4 12*s.* 6*d.*, it is now estimated to be £3 18*s.* 6*d.*; that of a ton of maize is reduced from £1 11*s.* to £1 5*s.* 1*d.* Of the Woburn experiments, in which "the manure from cattle foods of such widely different manure value as decorticated cotton-cake and maize have shown very little difference in the crops to which they were applied," the authors remark that "the result was doubtless due to the condition of the land being, in both cases, high enough to yield approximately maximum crops."

In addition to the revised table of original manurial value of the different foods after consumption by fattening animals, the authors now attempt an estimate of the compensation value or unexhausted manurial value of the same foods, after they have been used for a series of years by the outgoing tenant, and he has realised a certain portion of the manure value in his increased crops.

In the case of all the foods except hays and straws, one-half of the original manurial value of the purchased food used during the last year of the outgoing tenant's possession is to be deducted, and the remainder is the unexhausted manurial value. The unexhausted value of foods used the year before is one-third less than this; and one-third is deducted from the remainder for every additional year up to the eighth year before quitting. In the case of hays and straws, the constituents of which more slowly become available to crops, two-thirds of the original manurial value is deducted for the last year, and only one-fifth from year to year for each preceding year up to the eighth. For the many circumstances which must be taken into account in attempting to utilise the authors' tables, the original paper must be consulted; the principle, however, on which emphasis is laid, is the substitution of manurial value for cost of purchased foods as the basis of valuations. J. M. H. M.

Analytical Chemistry.

Apparatus for Operations in a Vacuum. By N. v. Klobukow (*Zeit. anal. Chem.*, **24**, 395—399).—A convenient arrangement for performing filtrations, washings, evaporations, &c., in a vacuum, or an atmosphere of carbonic anhydride, &c.

Estimation of Lithium by Spectrum Analysis. By B. K. Hofmann (*Ber.*, **18**, 2897—2898).—A question of priority.

Volumetric Estimation of Chlorine. By E. Bohlig (*Zeit. anal. Chem.*, **24**, 408).—This method, which depends on the insolubility of silver oxalate in neutral solutions and its immediate conversion into silver chloride in contact with soluble chlorides, is conducted as follows:—The liquid to be examined is boiled with magnesium carbonate, and filtered, an aliquot part of the clear solution is shaken up with dry silver oxalate, allowed to remain for a time, and again filtered; the filtrate is then treated with sulphuric acid, and titrated with decinormal permanganate solution (1 c.c. = 0·007 gram of chlorine), a correction being made for the solubility of the silver oxalate. The author has employed the method for the estimation of chlorine in water. When organic matter is present, the oxalic acid is first precipitated as the calcium salt, washed, and then titrated as before. A. P.

Detection of Chlorides in the Presence of Bromides and Iodides. By L. L. DE KONINCK (*Zeit. anal. Chem.*, **24**, 376—379).—Slight excess of silver nitrate is added to the solution, the precipitate collected, well washed, and digested with ammonium carbonate, which partially dissolves out any silver chloride present; on adding potassium bromide to the clear solution obtained, a distinct precipitate of silver bromide is formed if chlorides are present; a slight cloudiness is however always observed, and must therefore be neglected. If iodates are present, the silver precipitate must be treated with sulphurous acid, before proceeding with the examination. In the presence of cyanides, the silver precipitate must be heated sufficiently to destroy all the cyanogen, and then reduced with zinc or cadmium and dilute sulphuric acid, and the liquid examined as above. Sulphur compounds do not affect the process. A. P.

Kjeldahl's Method of Estimating Nitrogen. By T. PFEIFFER and F. LEHMANN (*Zeit. anal. Chem.*, **24**, 388—393).—The hydrogen given off from the zinc employed to prevent bumping in this process, carries over some of the alkali into the standard acid, causing an error of from 2·5 to 5·0 mgrms. of nitrogen; this may be avoided by introducing a short wide tube containing glass beads, above the distillation flask. In blank experiments performed with this modified apparatus, theoretical results were obtained. A. P.

Detection of Nitric Acid by Means of Pyrogallol. By CURTMAN (*Arch. Pharm.* [3], **23**, 711).—A little pyrogallol is dissolved in the water to be tested (less than 1 mgrm. to 1 c.c.); and 10 to 12 drops of concentrated sulphuric acid are dropped down the side of the test-tube, so as to form two layers. At the surface of contact, a brown or yellow coloration appears if nitric acid is present. 0·1 mgrm. of nitric acid in 1 litre of potable water can thus be clearly detected. J. T.

Estimation of Carbonic Anhydride. By KRATSCHMER (*Zeit. anal. Chem.*, **24**, 409).—A modification of Fresenius' absorption apparatus.

Estimation of Potassium Chlorate in Organic Mixtures. By SCHACK and SCHWARZ (*Arch. Pharm.* [3], **23**, 596).—Schack treats urine by completely precipitating with lead acetate, removing the excess of lead by hydrogen sulphide, and excess of the latter by boiling. The amount of chlorate is then deduced from the difference in the amount of chloride in the filtrate before and after ignition. The same process serves to estimate potassium chlorate in broth, but it fails in the case of strongly decomposed blood.

Schwarz proceeds as follows with urine:—A measured volume is boiled to coagulate albumin, made up to the original volume with water, and filtered. A portion is placed in a well-stoppered glass flask, some potassium iodide is added, and then hydrochloric acid to strongly acidify the liquid. After digestion on the steam-bath for about 15 minutes, the separated iodine is titrated with sodium thiosulphate, using zinc-iodine-starch solution as indicator. In the

case of the contents of a stomach, blood, &c., after dilution a dialyser is employed. The solution obtained is concentrated, and treated as in the case of urine. J. T.

Volumetric Estimation of the Alkaline Earths, and of Combined Sulphuric Acid. By O. Knöfler (*Annalen*, **230**, 345—367).—Calcium, strontium, and barium may be estimated by a modification of the process described in Mohr's *Lehrbuch der Titrirmethode*. Sufficient hydrochloric acid is added to the substance to produce a faintly acid reaction, and the solution is boiled to expel carbonic acid. A mixture of phenolphthalein and methyl-orange (1 gram of each dissolved in 250 c.c. of alcohol) is used as the indicator. One-fifth normal sodium carbonate solution is now added until a pale rose coloration is produced. Another cubic centimetre of the sodium carbonate solution is added, and the mixture is filtered through a wet filter-paper. The precipitate is washed once with water, and the excess of alkali in the filtrate determined by means of $\frac{1}{5}$ normal solution of hydrochloric acid. The volume of sodium carbonate solution, less the volume of acid, gives the amount of alkaline earth.

In the volumetric estimation of combined sulphuric acid, a $\frac{1}{5}$ normal barium chloride solution is required. The solution of the substance is acidified by the addition of $\frac{1}{5}$ normal acid, and boiled. Sufficient $\frac{1}{5}$ normal sodium carbonate solution is added to produce a distinctly alkaline reaction. The barium chloride solution is next added until the alkaline reaction disappears; an additional cubic centimetre is added, and the mixture boiled. The sodium carbonate is now added, and the analysis finished as in the determination of the alkaline earths. W. C. W.

Estimation of Tin in Hardhead. By R. Fresenius and E. Hintz (*Zeit. anal. Chem.*, **24**, 412—414).—3 grams of the finely-powdered sample are heated with aqua regia, the solution diluted and filtered, and the residue washed with water containing ammonium nitrate. The acid solution is made alkaline with soda, and digested with excess of sodium sulphide solution, the black precipitate formed, is collected on a filter and repeatedly extracted with further quantities of sodium sulphide solution; the residue is fused with liver of sulphur, extracted with water, and the filtered solution added to the alkaline sodium sulphide filtrate and washings; the whole is then acidified with hydrochloric acid, and the precipitated sulphides of tin, arsenic, antimony, tungsten, and molybdenum, thus obtained are treated with a solution of bromine in hydrochloric acid, whereby the greater part of the tungsten is removed as insoluble tungstic anhydride. The acid solution is evaporated to a small bulk with potassium chloride (to prevent loss of tin chloride by evaporation) any further deposit of tungstic anhydride being filtered off, and the tin is precipitated from the solution by ammonium nitrate, and purified from tungsten and molybdenum by repeated fusion with potassium cyanide. The metallic tin thus obtained, together with a small amount obtained in a similar manner from the precipitated tungstic anhydride, is again fused with liver of sulphur, extracted with water, filtered and acidified with sulphuric

acid; the precipitated sulphide is collected and ignited in a porcelain boat in a current of hydrogen, to remove sulphur and arsenic. The insoluble residue from this melt is heated in air, fused with potassium cyanide, and the small amount of tin obtained added to the main quantity, dried at 100°, and weighed. This tin still contains traces of silica, antimony, and arsenic, which are estimated by dissolving the tin in hydrochloric acid, and passing the gases given off through a silver solution, the insoluble matter and the antimony and arsenic found being deducted from the total. A. P.

New Reaction of Titanic Acid. By R. Fresenius (*Zeit. anal. Chem.*, **24**, 410—412).—When a solution of hyposulphurous acid is added to a solution of titanic anhydride in sulphuric or hydrochloric acid, an intense red coloration is produced which gradually changes to yellow and finally disappears, reappearing, however, on the addition of a further quantity of the reagent. Ether does not take up the colour from the solution. The reaction can be made use of only when other oxides or acids yielding coloured solutions on reduction are absent. Sulphurous and dithionic acids do not yield the reaction. A. P.

Analysis of Native Platinum. By T. Wilm (*Ber.*, **18**, 2536—2551).—A lengthy criticism of methods employed or suggested for the analysis of platinum ore. It appears that all the methods are inaccurate to a greater or less extent, the errors being mostly due to the different behaviour of these substances when mixed, to that which they exhibit when alone, and to the great energy with which many of the insoluble compounds, when precipitated, carry other substances down with them. No satisfactory method for this analysis is indicated. A. J. G.

Analysis of Gaseous Halogenated Hydrocarbons. By K. Seubert (*Ber.*, **18**, 2644—2655).—The author has experimented on the eudiometric analysis of some gaseous fluoro-, chloro-, and bromo-paraffins, and finds that by explosion with slight excess of oxygen under reduced pressure, they all yield carbonic anhydride and water; in the case of the fluorine compounds, hydrogen fluoride is also formed the chlorine compounds yield hydrogen chloride and a small quantity of chlorine, whilst the bromine compounds give bromine and a little hydrobromic acid. In the case of the chlorine and bromine compounds, therefore, the results are not very accurate. A. J. G.

Testing Peru Balsam. By A. Andrée (*Arch. Pharm.* [3], **22**, 561—576).—The author discusses various proposed methods as far as concerns tolu-balsam, benzoïn, and storax: the first two are detected with certainty by Hager's light petroleum process, when an increased resinous residue is obtained, with a corresponding diminution in the cinnameïn (benzyl cinnamate). The amount of acid in the cinnameïn will show whether tolu-balsam or benzoïn is the adulterant. Storax can be detected by Schlickum's ether-ammonia test, in which the ether layer gelatinises. Flückiger's test with lime is very good for the

detection of such adulterants as form compounds with the lime on rubbing up in the cold, but it does not detect tolu-balsam.

J. T.

Examination of Argol and Wine-lees. By F. Klein (*Zeit. anal. Chem.*, **24**, 379—388).—The total acidity is estimated in the usual manner. The total tartaric acid is estimated by Warington and Grosjean's method (this Journ., 1875, 973, and Trans., 1879, 341). The hydrogen potassium tartrate present is estimated by a modification of that process. A convenient amount of the sample is treated with hot water, filtered, and the solution and washings evaporated to about 40 c.c. 5 grams of potassium chloride are then added, the solution well shaken, and further treated as in Warington's process. From these results, the acid compounds other than hydrogen potassium tartrate, the calcium tartrate, and the hydrogen potassium tartrate present, may be calculated. The presence of calcium tartrate and hydrogen potassium phosphate does not affect the accuracy of the process. A. P.

Adulteration of Olive Oil. By A. Audoynaud (*Compt. rend.*, **101**, 752—753).—2 c.c. of oil is placed in a tube 150 mm. long and 15 mm. diameter, graduated in c.c., mixed with 0·1 gram of powdered potassium dichromate, agitated for a short time, then mixed with sufficient nitrosulphuric acid to increase the volume to 4 c.c., and again agitated. The liquid becomes brownish-red, and after the lapse of two minutes sufficient ether is added to increase the volume to 5 c.c., and the liquids are mixed by agitation. The liquid if left at rest tends to separate into two layers, but in a few minutes there is rapid effervescence, nitrogen oxides are given off, and the oil swims on the surface of the liquid with a peculiar colour.

With pure olive oil, the colour of the upper layer is green; but with any oil containing not less than 5 per cent. of oil of sesame, earth-nut, cotton-seed, or poppy, the colour varies from yellowish-green to yellow, or even reddish-yellow. The colour is more easily observed if 4—5 c.c. of water is added. C. H. B.

Reagent for Alkaloïds. By A. Luchini (*Arch. Pharm.* [3], **23**, 684).—The author suggests the use of a solution of potassium dichromate in concentrated sulphuric acid. He has compared it with Wenzell's solution with satisfactory results; the latter solution, as is known, consists of potassium permanganate dissolved in 200 parts of sulphuric acid. The two solutions together render unnecessary the use of the so-called general reagents for alkaloïds. 1—2 drops of the reagent are added to 1 c.c. of the alkaloïd or glucoside solution, and observations are finished after 24 hours. J. T.

Examination of Commercial Quinine Sulphate. By W. Koppeschaar (*Zeit. anal. Chem.*, **24**, 362—376).—The examination of commercial quinine sulphate is confined to the determination of the amounts of quinine and cinchonidine, as unless the sample has been adulterated, no other alkaloïds should be present. The method of separation of these alkaloïds by means of ether is practically worth-

less, as cinchonidine forms a compound alkaloïd with quinine, which is readily soluble in ether. In practised hands, the herapathite method yields very good results; but the most accurate method of determination is by a modification of Oudeman's process (*Annalen*, **182**, 67); the alkaloïds are converted into their tartrates, dried at 125—130°, and the specific rotatory power of the anhydrous salts determined. By using the anhydrous instead of the crystallised salt, errors are avoided due to variation in the amount of water of crystallisation present occurring from the formation of salts of a double alkaloïd. The percentage of quinine and cinchonine present may then be calculated by the formula $220{\cdot}07x + 137{\cdot}67\ (100 - x) = 100\ [\alpha]_D$, in which 220·07 and 137·67 are the respective specific rotatory powers of anhydrous quinine and cinchonidine tartrates.

Cinchonidine sulphate and quinine cinchonidine sulphate crystallise with 6 mols. H_2O, whilst quinine sulphate seems to crystallise with 8 mols. H_2O; the contradictory determinations of the water of crystallisation present in quinine sulphate, are probably due to the samples being indefinite mixtures of these salts. The author strongly recommends the introduction of acid quinine sulphate into commerce, as this sulphate may be readily purified from cinchonidine by recrystallisation. A. P.

Detection of Colouring Matters in Wine and Confectionery. By F. Strohmer (*Bied. Centr.*, 1885, 648).—To detect oxyazo-colouring matters, a sample of the liquid or an alcoholic extract of the solid is evaporated to one-half, so that nearly all the alcohol is dispersed. Pure wool is then boiled for 10 to 20 minutes in the liquid; the results will be as follows:—Ponceau R, dark-red; Ponceau RR, light-red; Bordeaux B, bluish Bordeaux red; Bordeaux R, reddish Bordeaux red; Crocein scarlet, violet-red; Bieberich scarlet, violet-red. If the dyed wool is dried and then moistened with concentrated sulphuric acid, the first two will be fiery-red, the next three deep indigo-blue, whilst the last will assume a dark-green colour. Pure red wine dyes wool a dirty brownish-red, which, under the influence of the acid, is changed to a dirty brown. E. W. P.

An Albumin Reaction. By D. Axenfeld (*Arch. Pharm.* [3], **23**, 715).—Many organic substances reduce gold chloride with the production of bluish, violet, or brown precipitates of gold; albumin, however, behaves differently in a solution acidified with formic acid. If to such a solution, some drops of a solution of gold chloride (1 : 1000) are added, gas bubbles appear on the walls of the vessel, the solution becomes rose-red; on further addition, purple-red, then bluish, and finally dark-blue; whilst on still further addition a blue flocculent precipitate appears, and the supernatant fluid becomes colourless. 1 gram of albumin solution containing 1 part per million with one drop of formic acid, gives with one drop of gold chloride solution a rose-red colour, with two drops a clear red, and with a third drop a blue colour. All albuminous compounds give these reactions. Gum solution gives a beautiful purple-red colour, but this becomes a splendid orange yellow on adding potash or soda. The

presence of other substances such as sodium chloride, uric acid, urea, and grape-sugar does not interfere with the reaction, but more acid and more gold solution are required. J. T.

Formation of Iodohæmin as a Method for Detecting Blood Stains. By BUFALINI (*Arch. Pharm.* [3], **23**, 682).—The author prefers the formation of iodohæmin to Teichmann's method. The blood, or the aqueous extract of blood stains, is treated with a drop of iodine tincture and very little acetic acid, a drop of the liquid is placed on a slide, and whilst this is repeatedly passed through a flame 8—10 drops of acetic acid are gradually added. In this way, crystals of iodohæmin can be obtained with absolute certainty in 1—2 minutes. J. T.

Technical Chemistry.

Preparation of Hydrogen. By F. HEMBERT and HENRY (*Compt. rend.*, **101**, 797).—Superheated steam is projected in fine jets on incandescent coke, and the mixture of equal volumes of hydrogen and carbonic oxide which is thus obtained is led into a second retort containing some refractory material so arranged that the gases pass over a very large heated surface. Steam heated to the point of dissociation is driven into this second retort, and the steam and carbonic oxide react on one another with production of carbonic anhydride and hydrogen, decomposition being facilitated by contact with the large extent of heated surface.

About 3200 cubic metres of hydrogen are obtained per ton of coke, and the cost is about 0·015 franc per cubic metre. C. H. B.

Apparatus for the Preparation of Carbonic Anhydride. (*Dingl. polyt. J.*, **258**, 181—182.)—A description of apparatus for preparing carbonic anhydride for technical purposes.

Action of Chlorates on Metallic Evaporating Pans. By G. LUNGE (*J. Soc. Chem. Ind.*, **4**, 32).—In order to determine the action of chlorate liquors on boiling-down pans, short pieces of cast-iron, wrought-iron, and lead tubing were separately immersed for seven hours in boiling solutions (I) of pure potassium chlorate containing 6·03 per cent. by weight, (II) of potassium chlorate containing 25 per cent., and (III) of calcium chlorate and calcium chloride obtained as usual by passing chlorine through milk of lime, and boiling to expel free chlorine and hypochlorite. The following results reduced to 1 square metre of surface were obtained :—

	Cast-iron.			Wrought-iron.			Lead.		
	I.	II.	III.	I.	II.	III.	I.	II.	III.
	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.
Metal oxidised.....	11·25	24·59	85·00	20·10	44·90	95·00	64·30	151·12	437·70
$KClO_3$ decomposed...	12·26	26·90	92·65	21·96	48·94	103·55	12·76	29·81	86·31

Since the quantity of chlorate destroyed is not essentially less in the case of lead than in that of iron, but the loss of metal dissolved is much greater with lead than with iron, boiling-down pans made of iron are preferable to leaden ones. There appears to be no essential difference between cast and wrought iron. D. B.

Rosolene. By E. Serrant (*Compt. rend.*, **101**, 953—955).—Rosolene or retinole, obtained in the distillation of colophony, boils at 280°, and is a heavy, dark-brown or dark-green oil with a strong tarry odour. It can be purified by redistillation with an equal volume of a dilute solution of an alkali, and subsequent treatment with litharge.

Rosolene closely resembles oil of poppy or sweet almond. It has a pale-yellow colour with a feeble violet fluorescence, a slight taste, and practically no odour. When taken internally, it acts simply as a mild purgative. Rosolene is insoluble in water or alcohol, but dissolves in ether, essential oils, and carbon bisulphide, and is miscible with fixed oils in all proportions. It does not saponify or oxidise and become rancid, and it has always a neutral reaction; sp. gr. 0·950.

Rosolene consists mainly of retinolene, $C_{16}H_{16}$, together with small quantities of terebene, colophene, altered resin, cresol, phenol, and their homologues. It combines the unguent properties of oils, fats, vaseline, &c., with considerable antiseptic power, and has also the advantage of not oxidising when exposed to air; it is a valuable cicatrix. C. H. B.

Power of Certain Salts to Decompose Tribasic Calcium Saccharate. By P. Degener (*Chem. Centr.*, 1885, 605).—The author has on a former occasion expressed the opinion that a portion of the loss of sugar in the separation as lime saccharate is due to the decomposition of this compound by salts of the alkali metals. Experiments with sodium butyrate, potassium sulphate, potassium oxalate, and citrate, show that these compounds have no such action.

P. P. B.

Fermentation of Bread. By A. Girard (*Compt. rend.*, **101**, 601—603).—The author has examined the gas contained in dough at various stages of preparation, and finds that it consists mainly of carbonic anhydride mixed with the air originally contained in the flour. In some cases, part of the oxygen has been absorbed, most probably in consequence of the secondary formation of acetic acid. When the dough is distilled with water, the distillate contains alcohol

in quantity amounting to 3·15 c.c., or 2·5 gram, per kilo. of paste. The same results were obtained whether the dough was mixed with leaven or with yeast, and it is evident therefore that what is termed the "rising" of the dough is the result of alcoholic fermentation.

C. H. B.

Formation of Basic Salts in the Saponification of Fats and Oils. By M. Dechan and T. Maben (*Pharm. J. Trans.* [3], **15**, 1025—1027).—Experiments are described which show that a soap will combine with more alkali than is required by the fatty acids present to form normal salts. The experiments prove that these fatty acids combine with varying proportions of alkalis, and from certain theoretical considerations, the authors conclude that basic salts are formed. This fact would go far to explain the great variations which soaps show in the amount of alkali they contain; and as these basic salts would be decomposed by water, producing free alkali and salts of the fatty acids, their presence in a soap would elucidate the liberation of free alkali when alcoholic solutions of some soaps are treated with water.

Moreover, the soaps containing the largest excess of combined alkali above that required to form the normal salts, have the strongest detergent powers, whilst those containing more normal proportions of fats and alkali have low cleansing properties, but are well suited for fulling or milling purposes. These facts are of great importance, as liberation of alkali during the dyeing of both silk and wool is very injurious. In the analysis of ten samples of hard and two of soft soap, the extreme variations per cent. of the alkalinity in relation to the acidity assumed to be oleic were as follows:—

	Fat.	Combined alkali.	Free alkali.	Combined alkali in excess.	Total excess of alkali.
Hard..	68·0—24·8	9·3—6·45	0·99—trace	3·17—0·03	4·16—0·26
Soft ...	65·0—41·0	11·1—9·4	1·41—0·3	2·60—0·31	4·01—0·61

D. A. L.

Preparation of Canarine. By H. O. Miller (*Dingl. polyt. J.*, **257**, 431).—This substance is prepared in the following manner:—3 kilos. of potassium thiocyanate dissolved in 6 litres of hot water, are treated with 300 grams of potassium chlorate and 2·4 kilos. of hydrochloric acid. After the reaction is ended, the mass is cooled, the remaining 1·2 kilos. of potassium chlorate and 3·6 kilos. of hydrochloric acid are then added gradually. The orange precipitate thus obtained is washed with hot water, pressed, and dried. It is then purified by solution in potash, filtration, and addition of alcohol to the filtrate, when the potassium compound is thrown down in the form of a reddish-orange crystalline precipitate. This is collected on a filter, washed, pressed, and dried. It is now dissolved in water, and the solution treated with hydrochloric acid, a brown precipitate of

canarine being obtained, which is filtered off, washed, and dried. *Canarine*, $C_6N_4O_2H_2S_5$, is insoluble in water, alcohol, and acids. It dissolves in concentrated sulphuric acid with evolution of sulphurous anhydride, and decomposes alkaline carbonates and earths, forming salts of the formula $C_6N_4O_2M_2H_2S_5$, whose aqueous solutions impart to cotton-colours varying from orange to maize-yellow, and resisting the action of light and extreme soaping. D. B.

Preparation of a Brown Azo-dye. (*Dingl. polyt. J.*, **257**, 435).—According to a process patented by P. Monnett and Co., a brown dye is obtained by the action of metaphenyleuediamine on diazotised phenylenediamine. D. B.

Producing Sulpho-colouring Matters by Electrolysis. By Ewer and Pick (*Dingl. polyt. J.*, **258**, 42).—When two plates of platinum are immersed in a solution of paramidodimethylaniline in dilute sulphuric acid, and the solution is saturated with hydrogen sulphide, the liquid round the positive plate (anode) assumes a blue colour, whilst hydrogen is liberated at the cathode. The blue colour soon disappears, and a grey film is deposited on the plate. When this coating is removed, the blue colour is again developed, so that if the plate is kept clean by constant brushing, a point is soon reached at which the whole of the hydrogen sulphide disappears from the solution, and the latter assumes a permanent blue colour. The solution at this stage consists mainly of methylene-white. As the electrolytic operation proceeds, the colour of the solution becomes deeper and deeper, until the conversion is completed. D. B.

New Blue for Printing. By E. Ullrich (*Dingl. polyt. J.*, **257**, 379).—Indulines have recently been brought into commerce in the form of a paste by the *Farbwerke, vormals Meister Lucius und Brüning*. When fixed with tannin, these dyes resist the action of light and soap better than the other basic colour derivatives. On decomposing the tannate formed on the fibre by prolonged boiling with caustic soda, the colour remains unaltered. The goods may then be boiled in comparatively strong mineral acids without detriment to the dye. This treatment appears to add brightness to the colour, from which it is inferred that salts of mineral acids give better results than tannates. Finding that the solubility in alcohol could not be applied to the fixing of this dye, a substance was sought for which would act as a solvent during the dyeing process, and thus effect the combination of the colour with tannin. Acetic acid, although at first used, was soon abandoned owing to its great volatility. Lactic acid gave better results, the high price, however, prevented its general application. Brandt then found that ethyl- or methyl-tartaric acid could be employed with advantage as a substitute for acetic acid. These acids are prepared on a commercial scale by Goldenberg, Geramont, and Co. D. B.

Bleaching Vegetable Fibres. By J. B. Thompson and J. P. Rickmann (*Dingl. polyt. J.*, **257**, 484).—It is proposed to treat vegetable

fibres with aluminium hydroxide and sodium carbonate, or kaolin and caustic soda. After five to six hours' digestion at a boiling temperature, the goods are rinsed and bleached with chloride of lime, in conjunction with carbonic anhydride. D. B.

Bleaching Vegetable Substances with Chloride of Lime. By G. Lunge (*Dingl. polyt. J.*, **257**, 387).—In order to augment the action of solutions of bleaching powder the author recommends the addition of small quantities of acetic or formic acid. In the case of acetic acid, hypochlorous acid and calcium acetate are first produced. In the bleaching process, the former gives up its oxygen, forming hydrochloric acid, which simultaneously acts on the calcium acetate, calcium chloride being obtained and acetic acid liberated. The latter is then allowed to act on fresh portions of bleaching powder.

D. B.

Bleaching and Dyeing Bone and Ivory. By R. Kayser (*Dingl. polyt. J.*, **257**, 436).—The bleaching is effected by means of hydrogen peroxide. The goods to be treated are cleaned with benzene or ether, and placed in a bath of equal parts of hydrogen peroxide and water. The dyeing is carried out in the following manner. Having cleaned the goods as before, they are immersed in a solution containing 10 grams of hydrochloric acid in 1 litre of water for two minutes, after which they are taken out and washed. For red, 10 grams of magenta or rubine are dissolved in 3 litres of water, and treated with 100 grams of acetic acid. The goods are then placed into this solution at a temperature of 50°. After half-an-hour's digestion they are taken out and washed, and dried at a gentle heat. The following solutions may be used under similar conditions:—For red: 5 grams of eosin, erythrosin, eosin-scarlet, phloxine, "rose Bengale," or "erythrine" dissolved in 1 litre of water and treated with 2 grams of tartaric acid. For violet: 5 grams methyl-violet or dahlia, dissolved in 1 litre of water and 3 grams of tartaric acid. For blue: two grams of methylene-blue or navy-blue. For green: 3 grams of new Victoria green or brilliant green, dissolved in two litres of water and 100 grams acetic acid. For yellow: 8 grams of naphthol-yellow S., or fast yellow, dissolved in 2 litres of water and 300 grams of acetic acid. For black: 30 grams of soluble nigrosin dissolved in 2 litres of water and treated with 300 grams of acetic acid. D. B.

Improved Gum Solution. (*Chem. Centr.*, 1885, 418.)—Two grams of crystallised aluminium sulphate dissolved in 20 grams water is added to 250 grams strong gum arabic solution (2 grams in 5 grams water). Ordinary solutions of gum arabic, however concentrated, fail in their adhesive power in many cases, such as the joining together of wood, glass, or porcelain; prepared, however, according to the above receipt, the solution meets all requirements.

J. K. C.

General and Physical Chemistry.

Absorption-spectrum of Oxygen. By N. Egoroff (*Compt. rend.*, **101**, 1143—1145).—The author gives a summary of previous observations on the absorption-spectrum of the terrestrial atmosphere and of oxygen, and reports the results of some recent experiments.

The absorption-spectrum of a layer of the atmosphere 3 kilos. in breadth, observed at St. Petersburg, showed the groups A, α, and B, but the group α was absent. The absorption-spectrum of a column of oxygen 60 metres in length, under a pressure of 6 atmos., showed distinctly the group A and the preliminary line and the seven doublets of the group B. It is evident therefore that all the lines in the groups A, B, and α in the absorption-spectrum of the terrestrial atmosphere are due to oxygen. C. H. B.

Band-spectrum of Nitrogen. By H. Deslandres (*Compt. rend.*, **101**, 1256—1260).—The band-spectrum of nitrogen consists of three distinct groups. The first, which is entirely visible, extends from λ7000 to about λ5000; the second, which is partly visible and partly in the ultra-violet, extends from about λ5000 to λ2800, whilst the third is wholly in the ultra-violet, and extends from λ3000 to λ2000. The second group is the most intense, and those bands of it which are visible are almost equal in intensity, but in the ultra-violet portion some are very intense whilst others are very weak. The two strongest bands in this group at 3579 and 3372 are characteristic of nitrogen, and can often be seen when all the other bands are invisible. The third group is less intense than the second, but has the same general appearance and shows the same succession of maxima and minima; it contains two very strong bands at 2480 and 2371 respectively.

If the nitrogen is perfectly free from oxygen, and the gas and the vacuum tube are completely dried by means of sodium, the third group of bands entirely disappears. It follows therefore that this group is due to an oxide of nitrogen. At the same time the first group showed no appreciable alteration, whilst the second group was distinctly stronger. The tube was not entirely free from hydrogen. If oxygen was allowed to enter the tube and was dried by means of sodium, the three groups were observed with their normal intensities. The second group is probably due to a compound of nitrogen and hydrogen (ammonia), whilst the first group seems to be due to nitrogen alone, or to some other compound of nitrogen and hydrogen.

C. H. B.

Relation between the Absorption and the Phosphorescence of Uranium Compounds. By H. Becquerel (*Compt. rend.*, **101**, 1252—1256).—The majority of the uranic compounds are phosphorescent, and the emitted light gives a spectrum which consists of seven or eight bands or groups of bands regularly distributed between C and F, the position and appearance of the bands depending on the

particular compound. The same compounds gave an absorption-spectrum of bands or groups of bands, which in position and appearance do not coincide with, but seem to be a repetition of, the spectrum of phosphorescence. The wave-lengths of all the bands in each spectrum are connected by the following law: the inverse differences of the wave-lengths, or the difference in the number of vibrations in unit time, is sensibly constant in passing from one group to another, and the value of this difference varies but slightly for the different uranic compounds. Each absorption-band corresponds with a group of radiations which excite phosphorescence, and the corresponding band in the spectrum of phosphorescence is of lower refrangibility. There are however always one or two bands common to both spectra, showing that in these regions the phosphorescent substance emits waves of the same length as those by which it was excited. The less refrangible portion of the absorption-spectrum of uranium compounds seems to terminate between F and *b*.

Uranous compounds show no appreciable phosphorescence, but give a remarkable discontinuous spectrum extending from F to a considerable distance into the infra-red. The spectra given by the solid salts are different from those of their aqueous solutions. The absorption-bands of the uranous compounds follow with remarkable regularity the law of distribution of bands in the spectrum of phosphorescence of the uranic compounds, but without having the same relative intensities. C. H. B.

Spectroscope for Furnaces and for the Bessemer Process. By C. V. Zenger (*Compt. rend.*, **101**, 1005).—Description of the arrangement of spectroscopic apparatus for the study of flames from various processes.

Electromotive Force of the Currents yielded by Metallic Couples in Simple Saline Solutions. By B. C. Damien (*Ann. Chim. Phys.* [6], **6**, 289—313).—From a large number of determinations of the E.M.F. of the currents yielded by zinc-copper and lead-platinum couples in various simple saline solutions, the author finds that the E.M.F. as a rule decreases with the time the couple is immersed. In the case, however, of the zinc-copper couple in solutions of the chlorides, the E.M.F. at first slowly increases. The E.M.F. of the current yielded by a zinc-copper couple in a solution of magnesium sulphate is very constant, scarcely varying 0·017 volt during 12 months, and is not appreciably affected by changes either of the strength of the solution or of temperature. By introducing an exterior resistance of 20,000 ohms, the current becomes practically invariable, even when the couple is kept in circuit; the author proposes to employ this couple for the generation of currents of standard strength. The zinc-copper couple yields currents whose E.M.F. is almost identical for members of any class of salts containing a given acid, but varies greatly with a change of acids; amalgamation of the zinc slightly increases the E.M.F. at first, but it decreases more rapidly than is the case when unamalgamated zinc is employed. The current obtained from a platinum and amalgamated zinc couple

in dilute sulphuric acid has its maximum E.M.F. when its solution contains 30 per cent. of acid. A. P.

Electrical Conductivity of Carbon Compounds. By A. Bartoli (*Gazzetta*, **15**, 392—397, and 397—399, 400—403).—In these papers the general results are given of the examination of the electric conductivity of liquid carbon compounds, especially those containing nitrogen. To avoid the effects of polarisation, the determinations were made in **U** tubes, which were heated to a constant temperature. The amides and anilides and compounds derived from them by the substitution of hydrogen in the acid radicles by the halogens, give indications of conductivity, as also the amines, anilines, and the pyridine bases. The nitro-compounds are conductors, and the substitution of hydrogen by the NO_2 group increases the conductivity. All liquid carbon compounds, whether in the pure state, or mixed or dissolved, show an increase of conductivity with rise of temperature, thus differing from metallic conductors.

A remarkable exception to this generalisation is diethylamine, the conductivity of which decreases with the temperature. Thus experiments are quoted to show that the relative conductivities at 10° and 56° are as 10·79 : 4·4. The conductivity of propylamine, allylamine, and amylamine between 0° and 50° is invariable.

In a former memoir, the author has shown that the electric conductivity of most solid carbon compounds diminishes very considerably at the immediate point of solidification, whilst in others this change, although still considerable, is more gradual. In this paper examples are given of the latter case, such as benzamide, phenol, and paratoluidine, and one, paranitrotoluene, of the former. Thus the relative conductivities of this last substance, which melts at 54°, are at 56° and at 50° in the ratio of 10 : 1 respectively. In conclusion, the author expresses his belief that the more regular gradation in the diminution of the conductivity is due not to retained traces of impurities, but to the actual nature or physical aggregation of the substances themselves. V. H. V.

Electrical Conductivity of Mixtures of Organic Compounds. By A. Bartoli (*Gazzetta*, **15**, 410—417).—The author has noticed that, although generally the electric conductivity of carbon compounds diminishes almost to zero at or about their points of solidification, yet certain mixtures and solutions of these compounds show an increase of conductivity at temperatures below that of the solidifying point, and a subsequent decrease to zero at a lower temperature. This phenomenon is not noticeable in mixtures of natural origin, such as the oils, wax, balsams, and resins, but only in artificially prepared mixtures and solutions, such as naphthalene with one of its derivatives, naphthalene or paraffin with phenol, phthalic or benzoic anhydride and the acids of the acetic series.

In this paper, tables are given illustrating this phenomenon. As regards its explanation there are two possible cases to be considered, 1st, that of a mechanical mixture, such as paraffin in amyl alcohol

or acetic acid; 2nd, that of the mutual solution of the two components, such as naphthalene in one of its derivatives.

In the former case, the interdiffused liquid would have a constant conductivity independent of the temperature up to the point of its own solidification. A simple case of the latter is the solution of a small quantity of a conductor in an insulator; such a material shows two points of solidification, the one near to that of the more abundant constituent, the other immediately below. Between these two points there is a sufficient amount of conducting liquid interposed between the solid particles, to admit of the passage of the current; but this gradually diminishes with decrease of temperature. This explanation is not however valid for compounds such as phenol and benzamide, which possess a certain amount of conductivity at temperatures far below that of their solidification. V. H. V.

Heat of Combustion of Compounds of the Fatty Series. By LOUGUININE (*Compt. rend.*, **101**, 1061—1064).

	Heat of combustion.	
	1 gram.	1 gram-molecule.
Paraldehyde	6160·4 cal.	813172·8 cal.
Normal propionic acid	4957·8 „	366877·2 „
„ „ anhydride	5746·8 „	747084·0 „
Aldol	6214·3 „	546858·4 „

From these results it follows that—

$$3C_2H_4O = C_6H_{12}O_3 \text{ develops } + 26827 \text{ cal.}$$

and $$C_6H_{10}O_3 + H_2O = 2C_3H_6O_2 \quad \text{„} \quad + 13330 \text{ „}$$

The conversion of acetic anhydride into acetic acid develops 13060 cal.

The aldol employed in these experiments was burnt as soon after preparation as possible. From the results obtained, it follows that the conversion of 2 mols. aldehyde into aldol develops + 13142 cal. Aldol is isomeric with isobutyric acid, but they have a different chemical function, and the difference between their heats of combustion, 29079 cal., is much greater than the differences found in the case of isomerides of the same function. C. H. B.

Heats of Combustion of Ethereal Salts of Fatty Acids. By LOUGUININE (*Compt. rend.*, **101**, 1154—1156).

	Heat of combustion.	
	1 gram.	1 gram-molecule.
Ethyl lactate	5559·4	656000·9
Ethyl citrate	5288·0	1459708·0
Ethyl butyrate	7338·4	851254·4
Ethyl isobutyrate	7290·7	845721·2

From these results the heats of combustion of the acids have been

calculated according to Berthelot's law, that the heat of combustion of the acid is equal to that of the ethereal salt, minus the sum of the heat of combustion of the alcohol radicle and the product of the number of molecules of alcohol into 2000 cal. The heats of formation of the acids are the differences between their heats of combustion and the sum of the heats of combustion of their constituents.

	Heat of combustion. 1 gram-molecule.	Heat of formation. 1 gram-molecule.
Lactic acid.....	329509	166451
Citric acid.....	480209	274991
Butyric acid.....	524764	—
Isobutyric acid.....	519221	—

The heat of combustion of normal propionic acid is 366877, and it follows that the replacement of H by OH with formation of lactic acid causes a diminution of 37368 cal. in the heat of combustion. The conversion of normal propyl alcohol into normal propyl glycol diminishes the heat of combustion by 49142 cal., and the corresponding value in the case of the iso-derivatives is 42014 cal. The conversion of normal propyl glycol into glycerol is accompanied by a decrease of 38716 cal. in the heat of combustion.

The author's value for the heat of combustion of normal butyric acid is considerably higher than that given by Favre and Silbermann (496940 cal.). The heats of combustion of the normal and iso-derivatives are practically identical. A direct determination of the heat of combustion of isobutyric acid gave the number 517796 cal.

C. H. B.

Do the Static and the Dynamic Methods of Measuring Vapour-tensions give Different Results? By G. W. A. Kahlbaum (*Ber.*, **18**, 3146—3153).—A reply to Ramsay and Young (compare this vol., p. 5).

Alcohol and Mixtures of Alcohol with Water. By G. T. Gerlach (*Zeit. anal. Chem.*, **24**, 487—533).—The author reviews the principal investigations which have been made of the physical properties of alcohol and its mixtures with water. Following a suggestion of Ilges, he shows that the following expression serves to connect the composition, specific heat, and boiling point of an alcohol water mixture:—

$$\frac{a \times s \times S + (100 - a)100^{\circ}}{100W} = \text{boiling point of the mixture,}$$

where a is the percentage of alcohol, W the specific heat of the mixture, s and S the specific heat and boiling point of absolute alcohol: the expression does not appear to be a general one, as it does not hold good for mixtures of sulphuric acid and water.

The following law appears, however, to connect the boiling point with the relative proportions in a mixture of two volatile substances.

If to an invariable quantity of the constituent of higher boiling

point varying quantities of the other constituent are added, the amount of the latter divided by the resulting depression of the boiling point gives a series of numbers having constant differences for equal increments of the more volatile substance. Moreover, the difference between each of the numbers of this series, and the corresponding one obtained by using as divisor the whole difference between the boiling points of the two constituents, is sensibly constant for a wide range, although, naturally, as the proportion of either constituent approaches infinity, the difference must fall to zero. Alteration of pressure affects the amount of the differences, but not their constancy. Mixtures of alcohol with water, glycerol with water, sulphuric acid with water, and alcohol with ether are found to follow this law; but it is obviously only applicable to mixtures whose boiling points lie between those of their constituents, and this is by no means always the case.

M. J. S.

The Law of Density Numbers. By J. A. Groshans (*Phil. Mag.* [5], **20**, 19—29 and 191—203; also *Rec. Trav. Chim.*, **4**, 236—262). —In these papers, the *law of density numbers* is enunciated and applied to the elements and their compounds in different states of physical aggregation, such as gases, liquids at their boiling points, and crystalline solids, whether hydrated, anhydrous, or in solution. Various relations are also indicated between these *density numbers* and the atomic weights, the specific gravities of solids and liquids, specific volumes, and the absolute boiling points.

Briefly expressed the law is as follows:—"*The specific gravities of substances are proportional to the density numbers.*"

Thus, to take a simple example in the case of two comparable compounds containing carbon, hydrogen, and oxygen only, of formulæ $C_pH_qO_r$ and $C_{p'}H_{q'}O_{r'}$, let n and n' be the sum of p, q, r, and p', q', r' respectively, then if their specific gravities be d and d', then—

$$\frac{d}{d'} = \frac{n}{n'} \text{ or } \frac{n}{d} = \frac{n'}{d'} = k \text{ a constant.}$$

These density numbers are simple integers; to each element is assigned only one such number, although two or more elements may have the same number. The following table contains some of the better ascertained numbers for the elements:—

H	1	Li	2	B	3	F	4	Mg	5	Ca	7	As	8	Cr	9	Ni	11
C	1	Be	2	N	3	Na	4	K	5			Se	8	Mn	9	Co	11
O	1	S	2	P	3	Al	4							Fe	9	Cu	11
						Si	4							Br	9	Zn	11
						Ce	4										

Sr	13	Sn	14	Ag	16	Ba	19	Hg	26	Pb	29
Sb	13	Te	14	Cd	16						
		I	14	Pt	16						

The various applications and relations alluded to above of these numbers will be discussed *seriatim*.

(i.) *Relation to Atomic Weights.*—In some few cases, pairs of ele-

ments, whose atomic weights differ by a constant quantity, show a similar constant difference between their density numbers; in other cases these numbers show a periodic variation with the atomic weights analogous to that observed in other physical constants.

(ii.) *Application to Hydrated Crystalline Salts.*—If B represent the sum of the density numbers of the elements contained in the salt, d its specific gravity, then $B/d=k$, a constant for all salts with similar formulæ, and containing the same number of molecules of water of crystallisation. Thus, referring to the above table, it is seen that for the salt $CaCl_2,6H_2O$, $B = 7 + 2 \times 4 + 6 \times 3 = 33$, $d = 1{\cdot}654$, $B/d = k = 19{\cdot}95$, and this constant holds good for other hexahydrated metallic chlorides, as also for the hexahydrated nitrates of nickel and zinc. So also for the double sulphates and selenates of ammonium and the metals of the magnesium series, the values for k are 28·7 and 29·5 respectively, which become 23·5 and 24 when the ammonium is replaced by potassium. In a series of tables, similar results are given for simple hydrated sulphates, the double silico-, stanno-, and zircono-fluorides, and the platino- and palladio-chlorides.

(iii.) *Relation to Absolute Boiling Points and Vapour-densities at that Point.*—If the boiling point of a compound be $s°$ and D_s the vapour-density at that point under standard conditions of pressure, then $T = 273 + s°$; with these factors the laws of Avogadro and Gay-Lussac may be expressed thus: $\frac{D_s}{D'_s} = \frac{M}{M'} \times \frac{T'}{T}$, in which M and M′ are the molecular weights of the two compared compounds. But from the law of density numbers $\frac{D_s}{D'_s} = \frac{B}{B'}$, hence $\frac{TB}{M} = k$ a constant, or if the compound contain carbon, hydrogen, and oxygen only, then $\frac{T \times n}{M} = k$, in which n is the sum of the number of atoms (cf. *supra*). Thus, in the case of water, this constant equals $62{\cdot}2 = \frac{(273 + 100)3}{18}$, and this constant equally holds good for other compounds derived from water by the replacement of hydrogen by hydrocarbon and acidic groupings, and containing 10 atoms of hydrogen. Similarly other series of compounds, isologous as regards the numbers of hydrogen-atoms contained therein, have similar constants.

(iv.) *Relation between the Values of the Constant* $T \times n/M$.—(i.) These constants form a series of algebraic numbers; (ii) in an homologous series the constants increase with increase of molecular weight; (iii) corresponding members of different homologous series, such as the ethers, ethereal salts of the acetic and oxalic acid series, and benzene, have the same constant. The numbers forming these series can be calculated according to the empirical formula $T \times n/M = 27{\cdot}8\sqrt{m}$, whilst in other cases the formula becomes $T \times n/M = 28{\cdot}7\sqrt{m + y}$, in which y is some small integer, whilst m represents the number of CH_2 groupings contained in the compound plus 1. Thus, the value for m for ethyl ether, $C_4H_{10}O$, is $4 + 1 = 5$; for benzene, C_6H_6, is $3 + 1 = 4$; for hexane, $C_6H_{14} = 7$.

(v.) *Determination of Absolute Boiling Points.*—It is obvious from

the above that if the values for m or $m + y$ be known for any series of compounds, then the absolute or actual boiling points can be calculated according to the formula $T = 273 + s = \frac{M}{n} 27{\cdot}8\sqrt{M}$. Thus, to take the example of benzene, $T = 273 + s = \frac{78}{12} \times 27{\cdot}8\sqrt{4}$ or $s = 88{\cdot}4$ (85 observed). The degree of accordance between the calculated and observed boiling points is illustrated by the following table, which is selected out of many given in the original papers.

Compound.	Boiling point calculated.	Boiling point observed.
Naphthylamine, $C_{10}H_9N$	298·5°	300°
Phenylamine, C_6H_7N	184·1	184
Nitronaphthalene, $C_{10}H_7O_2N$ ..	305·4	304
Nitrobenzene, $C_6H_5NO_2$	204·9	205
Methyl naphthyl ether, $C_{11}H_{10}O$	255·3	258
Methyl phenyl ether, C_7H_8O ..	146·6	152
Diphenyl, $C_{12}H_{10}$	241·9	240—243

Conversely from the observed boiling points the values for x in the above formula can be determined, as also the density numbers of other elements; tables are given illustrative of this point.

Relation to Specific Volumes.—As the specific volume of a liquid at its boiling point $s°$ is expressed by the formula $v_s = \frac{M}{d_s}$, in applying the law of density numbers to these volumes, the constant $v_s n/M$ analogous to Tn/M is obtained. From the data of Kopp, Pierre, and others the values for the constants in some few series are calculated, although the data are at present too few to admit of any discussion on the relations between the constants.

In conclusion, particular cases are discussed of certain isomeric substances, such as the crotonic acids, $C_4H_6O_2$, and compounds of the same or nearly equal molecular weight, and for which the value for n or B is the same, but whose boiling point and specific volumes are widely different, such as bromine and iodine monochloride, sulphur dichloride, S_2Cl_2, and sulphur oxychloride, SO_2Cl_2. In such cases it is observed that the values for x differ to an equal degree from some simple integer; thus this law points to a previously observed but incompletely understood disturbing influence. V. H. V.

Numerical Laws of Chemical Equilibrium. By H. Le Chatelier (*Compt. rend.*, **101**, 1005—1008).—A preliminary investigation of a general equation representing chemical change, in which the magnitude of the change is expressed as a function of the concentration (that is, the quantity of the reacting substances in unit volume), the temperature, and the electrical conditions. In gaseous systems, the coefficient of the proportional variation in the condensation of each substance taking part in the reaction, is equal to the mechanical energy gained by the system during an infinitely small transformation as a result of the disappearance of the particular

substance. The coefficient relative to the temperature is equal to the calorific energy gained under the same conditions.

The same formula should apply also to liquid systems, but the determination of the coefficients presents much greater difficulties.

C. H. B.

Cryoscopy as a means of Determining Molecular Weights. By F. M. RAOULT (*Compt. rend.*, **101**, 1056—1058).—The author's experiments have shown that the molecular reduction of the freezing point of one and the same solvent is practically constant for all substances belonging to the same type. Conversely, if the mean coefficient of reduction for several types are known, a determination of the coefficients of reduction of a given substance will serve to indicate which of two alternative molecular weights is correct.

Amongst organic compounds, if water is the solvent, and the substance is neither a true salt nor an ammonium, the molecular weight M is given by the formula $M = \frac{19}{A}$ where A is the observed coefficient of reduction; if acetic acid is the solvent, the formula becomes $M = \frac{39}{A}$; if benzene is the solvent and the compound is neither an alcohol, nor a phenol, nor an acid, the formula is $M = \frac{49}{A}$. The same formulæ hold good for anhydrous inorganic chlorides, such as $AsCl_3$, PCl_3, &c., which are soluble in benzene or acetic acid. The molecular weights of acids, bases, and salts can be determined in a similar manner, the proper constant being introduced into the formula in each case.

The same method serves to determine the basicity of an acid. If E is the weight of a normal alkaline salt which contains one equivalent of metal, and A its coefficient of reduction of the freezing point of water, then $A \times E = 35$ if the acid is monobasic, 20 if it is dibasic, and 15 if it is tribasic or tetrabasic.

Similarly, the atomicity of a metal can be determined. If E represents that weight of the nitrate which contains one equivalent of acid, then $A \times E = 35$ if the metal of the nitrate is monatomic, 22·5 if it is diatomic, and $A \times E < 22{\cdot}5$ if it is polyatomic. The same formulæ hold good in the case of the chlorides. C. H. B.

Physical Molecular Equivalents. By F. GUTHRIE (*Chem. News*, **52**, 232—233).—Many instances are adduced illustrating combinations of matter in which the mass ratios, although definite and constant, are apparently unconnected with molecular mass ratios. Such, for example, are the cryohydrates: thus sodium chloride forms $NaCl + 10H_2O$, but potassium sulphate cryohydrate is $K_2SO_4 + 114{\cdot}2H_2O$, whilst potassium nitrate yields $KNO_3 + 44{\cdot}6H_2O$. The sub-cryohydrates are, on the other hand, true molecular combinations. In alloys, when the metals are mixed in the proportions giving the lowest fusion points, they are never in atomic ratios; this also holds good with regard to the mass and molecular ratios of salt alloys. The varying solubility of salts in water of different temperatures is

referred to. Moreover, attention is drawn to the admixture of liquids with the production of heat, and subsequent contraction (chemical combination), or with cooling followed by a gain in volume (the antithesis of chemical combination); in the latter case, the maximum effect is produced at a certain molecular weight ratio (the ratio of maximum molecular repulsion), which, in the case of carbon bisulphide and chloroform, is 1 : 1, and in the case of carbon bisulphide and alcohol is 2 : 1; such mixtures have abnormally high vapour-tensions. In a mixture of carbonic anhydride and hydrogen, the joint volume is measurably greater than the sum of the volumes of the two gases alone. D. A. L.

Molecular Weights of Liquids and Solids (Evidence Deducible from the Study of Salts). By S. U. PICKERING (*Chem. News*, **52**, 239—240, 251—253).—In this paper the author criticises the literature connected with the so-called molecular compounds such as hydrated salts, basic salts, double salts, and with the numerous experiments on hydration, dehydration, vapour-tensions, dilatation, boiling points and densities of solutions, and calorimetric experiments made with such compounds. After carefully considering and sifting the evidence deducible from all these, and from the numerous experiments made by the author himself, he concludes "that, although in a few isolated cases the molecular weight would appear to be greater than the analytical results necessitate, still, in a vast majority of cases we have no grounds for multiplying these weights, and have, indeed, a considerable mass of evidence in favour of adhering to the simplest possible formulæ," but admits that although the smallest particles may be simple chemically, there is no reason why they "may not agglomerate and act in unison as regards certain physical forces," and hence "the molecule of the chemist is not necessarily identical with the molecule of the physicist." (Compare Guthrie, preceding Abstract). D. A. L.

Apparatus to Extract Solutions with Liquids. By G. NEUMANN (*Ber.*, **18**, 3061—3064).—An apparatus is described for extracting an aqueous solution with ether. Ether is boiled in a flask, from which the vapour passes nearly to the bottom of the vessel containing the liquid to be extracted; when the ether which rises to the surface of the liquid reaches a certain height, it syphons itself back into the distilling-flask. A second apparatus is also described. The author recommends the use of corks which have been brushed over with chromo-gelatin (prepared by adding 1 part of ammonium dichromate to a filtered solution of 4 parts of gelatin in 52 parts of boiling water), and then exposed to the light. Corks thus treated are attacked with difficulty by solvents. N. H. M.

Inorganic Chemistry

Influence of Moisture on the Oxidation of Hydrogen. By W. Müller-Erzbach (*Ber.*, **18**, 3239—3240).—The author has already shown (*Ann. Phys. Chem.*, **136**, 53) that ferric oxide requires a higher temperature for reduction in nearly dry hydrogen, than in moist hydrogen. When hæmatite is heated in sealed tubes with calcium chloride and hydrogen for 7, 17, and 37 hours respectively, one-half, one-third, and one-eighth of the hydrogen remained. This is explained by the gradual decrease of the amount of moisture in the tube, and the consequent retarding of the reduction. N. H. M.

Percentage of Oxygen in the Air. By U. Kreusler (*Bied. Centr.*, 1885, 649—654).—Having passed in review the labours of others, and especially those of v. Jolly, and having made numerous analyses of the air himself, the author comes to the conclusion that the statement that the composition of the atmosphere is constant remains unshaken, or at least, that the variation is of the very smallest kind. E. W. P.

Percentage of Sulphurous Anhydride in Aqueous Solutions of Various Specific Gravities and its Determination therein. By W. B. Giles and A. Schearer (*J. Soc. Chem. Ind.*, **4**, 303—305). In a previous communication (*ibid.*, **3**, 197), the authors gave an account of an accurate and rapid method of estimating the percentage of sulphurous anhydride when in combination with bases. They found it necessary to add the sulphite to the iodine solution, and not the iodine to the sulphite; and instead of diluting with water down to the percentage of 0·05 per cent. of SO_2, as recommended by Bunsen, better results were obtained by placing the weighed solid or liquid substance into an excess of decinormal iodine solution without the use of water. In the present paper, it is shown that the same method gives accurate results when applied to the estimation of the anhydride itself. The amount of sulphurous anhydride in its solutions of varying specific gravities was then determined, and is compared in the accompanying table with the figures given by Gautier and Wagner. From a large number of experiments, the authors have deduced the following simple law of the ratio between any given percentage of sulphurous anhydride in an aqueous solution at 15·4° and 760 mm. and its sp. gr. "The percentage of SO_2 multiplied by 5 gives the sp. gr. of the solution over and above 1000."

Percentage of SO_2 *in Solutions of various Specific Gravities.*

Giles and Schearer.		Gautier and Wagner.	
Sp. gr. at 15·5°.	SO_2.	Sp. gr.	SO_2.
1·0051	0·99	1·0028	0·5
1·0102	2·05	1·0056	1·0
1·0148	2·87	1·0113	2·0
1·0204	4·04	1·0221	4·0
1·0252	4·99	1 0275	5·0
1·0297	5·89	1·0328	6·0
1·0353	7·01	1·0397	7·0
1·0399	8·08	1·0426	8·0
1·0438	8·68	1·0474	9·0
1·0492	9·80	1·0520	10·0
1·0541	10·75	—	—

D. B.

Preparation of Nitric Oxide. By H. Kaemmerer (*Ber.*, **18**, 3064—3066).—A Woulff's bottle, fitted with a funnel and delivery tube, is filled loosely with strips of copper, and then one-third with a cold saturated solution of sodium nitrate. Strong sulphuric is added more or less quickly according to the amount of gas required. The evolution of gas is very regular, and may be kept up for hours.

N. H. M.

Action of Hydrogen Phosphide on Solutions of Metallic Salts. By P. Kulisch (*Annalen*, **231**, 327, and *Chem. Centr.*, 1885, 805—806).—The author's results disagree in general with Winkler's investigations (*Ann. Phys. Chem.*, **111**, 443). Hydrogen phosphide when passed through solutions of salts of the light metals, remains unchanged; the white precipitate, formed in some cases, consists simply of finely divided phosphorus carried over mechanically. Winkler's assumption that hydrogen phosphide does not reduce ammonium molybdate is incorrect, for although solutions of that salt free from acid are scarcely affected by the gas, yet free molybdic acid, especially when warmed, is reduced with formation of the intense blue compound of molybdic acid with molybdenum oxide; this reaction serves for the detection of traces of the gas. Solutions of salts of the heavy metals when treated with the gas undergo partial or total reduction, or a phosphide is formed; generally both reactions go on together, as in the case of copper sulphate, silver, cobalt, and nickel salts. Lead and cadmium salts furnish precipitates containing excess of metal, which cannot be separated from the phosphide; these mixed precipitates show a marked tendency to deposit in a mirror-like form. The properties of the phosphides obtained differ very much; when treated with strong acids they are decomposed, and, with the exception of cadmium phosphide, yield non-spontaneously inflammable gas. As a rule the action of the hydrogen phosphide is very slow.

H. P. W.

Hypophosphoric Acid. By A. Joly (*Compt. rend.*, **101**, 1058—1061 and 1148—1151).—Phosphorus partly immersed in water is

allowed to oxidise slowly in a confined space of air at the ordinary temperature, the acid liquid heated to boiling, mixed with sodium carbonate until neutral to methyl-orange, concentrated and allowed to cool. The salt which separates is washed with cold water and recrystallised from boiling water, when it forms large crystals identical with those of sodium hypophosphate, $Na_2H_2P_2O_6 + 6H_2O$, described by Salzer. It loses $6H_2O$ at 110°, and at a red heat is converted into sodium metaphosphate with evolution of hydrogen. Its solution gives with silver nitrate a white precipitate, which dissolves in warm dilute acid, from which $Ag_4P_2O_6$ crystallises on cooling.

Hypophosphoric acid resembles phosphoric and phosphorous acids in its behaviour towards methyl-orange and phenolphthalein, but differs from them in that it shows an intermediate state of saturation corresponding with the formation of a sesquisalt.

When a solution of monosodium hypophosphate is mixed with a solution of an equivalent quantity of barium chloride, a gelatinous precipitate is formed, and the solution, which was previously neutral to *Orange No.* 3, becomes acid to this indicator. Titration with standard alkali shows that half an equivalent of acid is liberated, and the precipitate is therefore dibarium hypophosphate. If the precipitate is left in contact with the liquid, it is gradually converted into crystals of monobarium hypophosphate—the conversion being accelerated by agitation and by heating to 50° or 60°. If the original solutions are mixed at 100°, the gelatinous precipitate almost immediately changes into a granular precipitate of the same composition, which is only very slowly attacked by the liberated acid. Monobarium hypophosphate is almost insoluble in water. It loses $2H_2O$ (10·8 per cent.) at 140°, and at a somewhat higher temperature gives off hydrogen which burns with a green flame. This salt can also be obtained in the following manner. A portion of the aqueous solution of the products of the slow combustion of phosphorus is titrated and the remainder is heated to boiling and mixed with sufficient barium carbonate to neutralise one-fourth of the total acid. When the liquid is allowed to cool monobarium hypophosphate crystallises out and is purified by washing with cold water until the washings no longer reduce silver nitrate, and is then recrystallised from very dilute boiling nitric acid.

In order to prepare the acid, the monobarium salt is mixed with an equivalent quantity of sulphuric acid diluted with its own weight of water. After standing for two or three days, the solution is evaporated in a vacuum over some hygroscopic substance, and when the composition of the liquid approaches $P_2O_4,6H_2O$, it deposits bulky, rectangular tables which probably belong to the rhombic system. These crystals have the composition $P_2O_4,4H_2O$, are deliquescent, and dissolve rapidly in a small quantity of water. With silver nitrate, the solution gives a white precipitate which does not blacken on boiling and is soluble in warm dilute nitric acid (1 : 1).

C. H. B.

Preparation of Phosphoric Acid. By G. A. Ziegeler (*Dingl. polyt. J.*, **258**, 239).—Phosphoric acid can be prepared from phosphorus and the quantity of nitric acid theoretically required by

adding a small amount of iodine to the mixture. For 100 grams of phosphorus 0·3 to 0·6 gram iodine is used. D. B.

Hydrates of Arsenic Acid. By A. Joly (*Compt. rend.*, **101**, 1262—1264).—The hydrate $As_2O_5,4H_2O$ is deposited in long, transparent prisms from a solution of the same composition if the latter is agitated or is exposed to winter temperature. If the solution is more dilute, a crystal of $As_2O_5,4H_2O$ or of the isomorphous $P_2O_5,4H_2O$ must be added to produce crystallisation. A solution having the composition $As_2O_5 + 5H_2O$ may be cooled to $-50°$ and violently agitated, without solidification taking place. The crystals of $As_2O_5,4H_2O$ melt at 35·5—36°, are very deliquescent, and dissolve rapidly in a small quantity of water with reduction of temperature. Heat of solution at 13° in $100H_2O = -2·8$ cal., in $300\,H_2O = -2·6$ cal., in $900\,H_2O = = -2·0$ cal. Heat of fusion $-7·4$ cal. It follows from these numbers and the heats of solution of the other hydrates as determined by Thomsen, that—

As_2O_5 solid	+ $2H_2O$ solid	develops	+ 1·90	cal.
As_2O_5 „	+ $3H_2O$	„	+ 2·6	„
As_2O_5 „	+ $4H_2O$	„	+ 2·8	„

combination with the last molecule of water develops only +0·2. The heats of hydration are much lower than in the case of phosphoric acid.

The crystals of the hydrate $As_2O_5,4H_2O$ effloresce rapidly in a dry vacuum, and form a white powder of the composition $2As_2O_5,3H_2O$. The same product is obtained by heating the hydrate, $As_2O_5,3H_2O$, at 100° until it ceases to lose weight. This sesquihydrate is only very slightly hygroscopic, but dissolves rapidly in water with development of heat. Heat of solution at 14° = +5·52, and therefore $2As_2O_5$ solid $+3H_2O$ solid, develops +2·20 cal. It follows from this result that combination with the first molecule of water develops more heat than combination with the second. When the hydrate $As_2O_5,4H_2O$ is melted in a closed vessel and allowed to remain in superfusion at the ordinary temperature, it gradually deposits crystals of the hydrate $As_2O_5,3H_2O$. This change is exothermic, and develops +5·8 cal.

The hydrate $As_2O_5,3H_2O$, whether obtained at the ordinary temperature or by Kopp's method at 100°, does not cause the solidification of superfused $P_2O_5,3H_2O$, and it would seem, therefore, that the trihydrates, unlike the tetrahydrates, are not isomorphous.

C. H. B.

Oxidation of Various Forms of Carbon. By A. Bartoli and G. Papasogli (*Gazzetta*, **15**, 446—457).—In this paper, an account is given of experiments on the oxidation by alkaline hypochlorites of natural and artificial forms of carbon, such as various species of lignites and fossil carbon, wood and animal charcoal, soot and lamp-black. As a general result it is shown that those forms of carbon which contain one or more per cent. of hydrogen are completely oxidised by alkaline hypochlorites with formation of carbonic anhydride, oxalic and mellitic acids, together with other less-defined substances. The

various forms of carbon are separable into four distinct classes: 1st, those mentioned above, oxidised by alkaline hypochlorites; 2nd, those unaltered by hypochlorites but transformed into soluble products by potassium chlorate and nitric acid, such as retort carbon; 3rd, those transformed by the latter reagent into the various forms of graphite; and, 4th, the diamond unaltered by any of the above reagents.

V. H. V.

Characteristic Equation of Carbonic Anhydride. By E. Sarrau (*Compt. rend.*, **101**, 1145—1148).—The characteristic equation of carbonic anhydride being put into the form

$$p = \frac{RT}{v - \alpha} - \frac{K\epsilon^{-T}}{(v + \beta)^2},$$

the constants have the values $K = 0{\cdot}016551$; $\epsilon = 1{\cdot}00285$; $\alpha = 0{\cdot}001150$; and $\beta = 0{\cdot}000703$; the two last values being calculated from the results of Cailletet and Hautefeuille's experiments on the density of liquid carbonic anhydride under varying conditions. The values calculated by means of these constants agree very closely with Cailletet and Hautefeuille's numbers, and also agree fairly well with the results of Andrews and Amagat's experiments on the gas.

By means of these coefficients and Clausius' tables, the following numbers have been calculated:—P = tension of the saturated vapour of carbonic anhydride at the temperature t; S and σ = respectively the specific volumes of the vapour and of the liquid under the pressure P, calculated to the normal volume of the gas; Δ = the density of the liquid:—

t ..	30°	10°	−10°	−30°	−50°
P..	73·49 atmos.	46·12 atmos.	27·02 atmos.	14·49 atmos.	6·91 atmos.
s ..	0·00568	0·01422	0·02706	0·05216	0·10795
σ ..	0·00428	0·00251	0·00208	0·00183	0·00167
Δ..	0·461	0·785	0·950	1·076	1·178

The numbers await experimental verification. At the temperature of solidification, −57°, the calculated value of P is 5·15 atmos., and of Δ 1·209. The actual tension measured by Faraday was 5·3 atmos.

C. H. B.

Limits of the Conversion of Sodium Carbonate into Sodium Hydroxide by Lime. By G. Lunge and J. Schmid (*Ber.*, **18**, 3286—3289).—According to Mitscherlich (*Lehrb. d. Chemie*, **2**, 15) 1 part of potassium carbonate is only completely causticised by lime in presence of 50 parts of water. Parnell and Simpson (Engl. Pat. No. 4144, Nov. 7, 1877) proposed operating with more concentrated solutions of sodium carbonate under pressure. Experiments made by the authors with solutions of pure carbonate of different strengths show that the highest percentages (99·4 and 99·3) are obtained by using a 2 per cent. solution of sodium carbonate. The employment of pressure has no material influence on the result; it is probable that a thorough stirring assists the reaction.

N. H. M.

A New Ammonium Magnesium Phosphate. By A. Gawalovski (*Chem. Centr.*, 1885, 721).—Precipitated ammonium magnesium phosphate is dissolved to saturation in acetic acid: the solution after a time deposits well-formed crystals having the composition $Mg_5(NH_4)_2(PO_4)_4 + 24H_2O$. C. F. C.

Some Properties of Zinc. By L. L'Hôte (*Compt. rend.*, **101**, 1153).—Perfectly pure zinc was obtained by mixing precipitated zinc oxide with calcined lamp-black and distilling the mixture *per descensum*. The pure metal does not decompose water at 100°, and is not attacked by dilute sulphuric acid.

If the pure zinc is melted in a crucible and stirred with an iron rod, it takes up 0·03—0·05 per cent. of the iron, and the impure zinc thus obtained decomposes boiling water and dissolves in dilute sulphuric acid. The presence of very small quantities of antimony or arsenic have the same effect on the properties of zinc. All commercial samples of the metal decompose water at 100°.

The author recommends the use of zinc containing a small quantity of iron in Marsh's process in order to insure a regular evolution of gas. C. H. B.

Action of Zinc-dust on Zinc Hydroxide. By G. Williams (*Chem. News*, **52**, 301).—In connection with the evolution of hydrogen from strongly heated zinc-dust (compare this vol., p. 15), it is now shown that zinc-dust which, when heated alone, yielded about 50 times its volume of hydrogen, when mixed with equal weights of zinc hydroxide and then heated to redness, gave off as much as 535 times its volume of hydrogen. D. A. L.

Action of Nitric Acid on Mercuric Iodide. By K. Kraut (*Ber.*, **18**, 3461—3462).—As it appears that the observations of Liebig and other chemists regarding the reaction between mercuric iodide and nitric acid were incorrect, the author has examined this point. Mercuric iodide when boiled with nitric acid of sp. gr. 1·5, is converted into the iodate $Hg(IO_3)_2$; the same result is obtained with acid of sp. gr. 1·4, although a small quantity of nitrate enters into solution; with acid of sp. gr. 1·3, white, micaceous leaflets of a compound, $HgI_2Hg(NO_3)_2$, separate, and finally, with acid of sp. gr. 1·2, red crystals of unaltered iodide are obtained together with white crystals of the preceding compound. V. H. V.

Aluminium Sulphate. By A. Gawalovski (*Chem. Centr.*, 1885, 721).—Perfect crystals of this salt are obtained by dissolving the freshly precipitated hydroxide to saturation in sulphuric acid and allowing the solution to remain for several months. The octahedra have the composition $Al_23SO_4 + 17H_2O$. C. F. C.

Preparation of Vanadyl Chloride. By L. L'Hôte (*Compt. rend.*, **101**, 1151—1152).—Vanadinite occurs in somewhat large quantity at San Luis Potosi, in Mexico. A sample of the mineral from this district had the composition—

$SiO_2 + A_2O_3$.	CaO.	Fe_2O_3.	MnO.	CuO.	PbO.	As_2O_5.	V_2O_5.	Loss.
13·20	5·48	3·08	1·57	10·01	43·08	0·46	14·42	8·70

In order to separate the vanadium, the powdered mineral is mixed with four times its weight of lamp-black, made into a paste with oil, and calcined. The calcined product is then heated in an oil-bath in a current of dry chlorine, care being taken to prevent the temperature exceeding 300°. Pure vanadyl trichloride begins to distil at 210°, and if the temperature is raised to 300° the whole of the vanadium in the mineral is converted into this compound. C. H. B.

Complex Inorganic Acids. By W. Gibbs (*Amer. Chem. J.*, **7**, 209—238).—*Phosphovanadates.*—Phosphoric and vanadic anhydrides unite to form well-defined complex inorganic acids strictly comparable with those containing phosphoric and molybdic or tungstic anhydrides (compare Abstr., 1884, 161, 560, 713; and 1882, 469, 702). The salts are crystalline, and have a yellow or orange colour; they are frequently decomposed by a large quantity of water, and are generally formed by treating a mixed solution of a vanadate and a phosphate with an acid. The following compounds are described:—

$P_2O_5,V_2O_5,(NH_4)_2O + H_2O$, bright yellow, granular crystals; $P_2O_5,V_2O_5,2Ag_2O+5H_2O$, granular, yellow crystals; $4P_2O_5,6V_2O_5,3K_2O + 21H_2O$, yellow, granular masses; $7P_2O_5,6V_2O_5 + 37H_2O$, distinctly crystalline masses; $P_2O_5,20V_2O_5 + 59H_2O$, granular ruby or garnet-red crystals; $P_2O_5,2V_2O_5,(NH_4)_2O + 7H_2O$, a lemon-yellow crystalline salt.

Arseniovanadates.—These compounds generally resemble the preceding salts. The compound $5As_2O_5,8V_2O_5 + 27H_2O$, a crystalline orange salt, is described; a second preparation had a different composition, namely, $7As_2O_5,6V_2O_5 + ?H_2O$ (compare Abstr., 1884, 1266).

Phosphovanadicovanadates are formed by adding a solution of vanadium dioxide, VO_2, in hydrochloric acid to a mixed solution of a vanadate and phosphate; they are well crystallised, dark green salts; $2P_2O_5,VO_2,18V_2O_5,7(NH_4)_2O + 50H_2O$ dissolves in water to a deep red solution; $5P_2O_5,VO_2,4V_2O_5,4Na_2O + 37H_2O$, green, crystalline scales, insoluble in water; $12P_2O_5,12VO_2,6V_2O_5,5K_2O + 40H_2O$, deep green crystals, appearing almost black;

$$12P_2O_5,14VO_2,6V_2O_5,7K_2O + 52H_2O,$$

green, crystalline salt; $14P_2O_5,16VO_2,6V_2O_5,7(NH_4)_2O + 67H_2O$, intensely deep green crystals: $10P_2O_5,11VO_2,5V_2O_5,(NH_4)_2O + 41H_2O$, lighter green in colour.

Arseniovanadicovanadates, $12As_2O_5,12VO_2,6V_2O_5,5(NH_4)_2O + 7H_2O$, very dark green, almost black, crystalline salt;

$$9As_2O_5,9VO_2,8V_2O_5,4(NH_4)_2O + 11H_2O,$$

olive-green in colour.

Vanadicovanadates are obtained by adding an acid solution of vanadium dioxide to a vanadate; they are generally dark green (compare Trans., 1886, 30). The salt $4V_2O_5,2VO_2,(NH_4)_2O + 8H_2O$ is described.

The probable existence of vanadium compounds corresponding with the phosphorosotungstates and hypophosphotungstates is indicated; and as there are ortho-, pyro-, and various meta-phosphotungstates, so there ought to exist corresponding vanadium compounds. It is suggested that the various double chlorides (such as $VOCl_3,PtCl_4$, &c.) are the chlorides of double oxides capable of forming complex acids: and that the ortho-, pyro-, and meta-vanadates, tungstates, &c., are only particular members of a homologous series. From the resemblance of the phospho-vanadates, -tungstates, and -molybdates, it appears that MoO_3, WO_3, and $V_2O_2{\cdot}O_3$ are chemically equivalent.

The description of two new *sodio-ammonium tungstates* is appended, namely, $3Na_2O,4(NH_4)_2O,16WO_3 + 18H_2O$ and

$$Na_2O,4(NH_4)_2O,12WO_3 + 14H_2O;$$

both form small shining scales. H. B.

Mineralogical Chemistry.

Native Arsenic of Valtellina. By D. Bizzari and G. Campani (*Gazzetta*, **15**, 349—351).—In this paper is described the first specimen of native arsenic in Italy, found on the mountain of Corna dei Darden, near the Passo del Gatto in the Valtelline. The following analytical results were obtained:—

Arsenic	89·57
Antimony	8·27
Sulphur, calcium, lead, silica, &c.	2·16

It occurred in steel-grey, compact masses, of sp. gr. at 27° = 5·777, hardness 4; it resembled the native arsenic of Marienberg.

V. H. V.

Doubly Refracting Crystals of Sodium Chloride and Potassium Chloride. By A. Ben Saude (*Zeit. Kryst. Min.*, **10**, 642—643).—Doubly refracting crystals of sodium chloride are obtained if the crystallisation is accelerated by change of temperature, or if a gelatinous substance is added to the solution, or if the solubility is decreased by the addition of alcohol. The doubly refracting crystals of sodium or potassium chloride are much less clear than the ordinary crystals; the clouding being caused by numerous rectangular tabular fluid-inclusions.

A mixture of sodium and potassium chlorides, slowly evaporated, gave crystals exhibiting double refraction. These crystals were quite free from inclusions. In the same way, according to Brauns (*Zeit. Kryst. Min.*, **10**, 110), in the case of the alums, an isomorphous mixture causes optical anomalies. B. H. B.

Zinc-blende. By F. Becke (*Zeit. Kryst. Min.*, **11**, 54—58).—Boiling dilute hydrochloric acid, after two to three minutes' action, produces etched figures on the crystalline faces of zinc-blende. They are trisymmetrical on the planes of the tetrahedron, and appear as depressed trilateral pyramids. Supported by the results obtained by thus etching zinc-blende with hydrochloric acid, the author compares the crystals from different localities, giving, in conclusion, a table of the 35 forms hitherto found to occur on zinc-blende crystals.

B. H. B.

Parallel Growth of Tetrahedrite and Zinc-blende. By F. Becke (*Zeit. Kryst. Min.*, **11**, 53—54).—At Kapnik, on compact brown blende and tetrahedrite, yellowish-brown partially transparent crystals of blende occur. On the blende crystals are planted numerous tetrahedrite crystals, mostly less than 2 mm. in size. They are younger than the blende, and not a product of its alteration. Tetrahedrite and blende are associated according to this law: the principal axes are parallel, the first tetrahedron of the tetrahedrite is parallel to the second tetrahedron of the blende. B. H. B.

So-called Nepaulite. By F. R. Mallet (*Rec. Geol. Surv. India*, 1885).—The name nepaulite was given by Piddington to a mineral from Khatmandu which he considered to be essentially a carbonate of bismuth, copper, and iron. The author has re-examined the mineral, and finds that on analysis it gives—

S.	Sb.	As.	Cu.	Ag.	Pb.	Fe.
21·12	25·17	1·32	38·69	trace	0·3	5·33

Zn.	$CaCO_3$.	$MgCO_3$.	Insoluble.
2·44	1·07	0·13	0·68

It would therefore seem to be a partially altered tetrahedrite.

Artificial Production of Sulphides. By C. Doelter (*Zeit. Kryst. Min.*, **11**, 29—41).—*Iron Pyrites.*—The repetition of the synthetical experiments of Durocher and Rammelsberg, in which iron chloride or iron glance was acted on by hydrogen sulphide at a red heat, showed that a temperature of 200° is sufficient. The experiment was successful when ferric oxide was employed instead of iron glance or metallic iron, but failed with iron carbonate and ferrous sulphate. In the latter case, troilite appears to be formed. The crystal form of artificial pyrites is usually the cube or the combination of cube and octahedron.

In order to show the action of water containing hydrogen sulphide on iron oxides, iron glance, magnetic oxide, and lastly siderite were treated with aqueous hydrogen sulphide in a closed tube for 72 hours at 90°. The best result was obtained with siderite, minute crystals of pyrites being formed. These crystals contained 46·07 per cent. of iron and 53·13 per cent. of sulphur. The results of the three experiments showed that ferric oxide, iron carbonate, and magnetic oxide may easily pass over into pyrites by the action of aqueous hydrogen

sulphide in a short time with an inconsiderable increase of temperature.

Marcasite.—By mixing ferrous sulphate with a little carbon and heating to a red heat in a stream of hydrogen sulphide, marcasite was not formed. The same negative result was obtained by reducing iron carbonate with sulphuretted hydrogen, and by decomposing ferrous sulphate with illuminating gas. In all three cases iron pyrites or troilite was formed.

Hauerite and Manganese-blende.—If hydrogen sulphide is allowed to act on various manganese compounds, manganese-blende, MnS, is formed. To obtain hauerite, the sulphur must consequently be in excess. The author mixed sulphur with the manganese compound, and warmed the mass in a stream of hydrogen sulphide. The results with braunite, manganese chloride, and potassium permanganate were unsuccessful, manganese-blende being formed. With a mixture of pyrolusite and sulphur, hauerite was obtained.

Galena.—The author's experiments show that galena can easily be formed in nature by the action of hydrogen sulphide on solutions of lead carbonate, or lead chloride. Galena was produced at the ordinary temperature by exposing lead chloride to the action of hydrogen sulphide and some sodium hydrogen carbonate for five months.

Cinnabar.—The occurrence of mercury ores shows that they must apparently, in many cases, have been formed by the action of hydrogen sulphide at a low temperature. This is confirmed by a simple experiment; mercury heated in a water-bath at 70° to 90° for six days in a tube filled with hydrogen sulphide, forms small, red crystals of cinnabar.

Covelline and Copper Glance.—Copper oxide treated with hydrogen sulphide at a temperature of 200° gives a very characteristic crystalline aggregate of covelline. At a higher temperature (250 to 400°) copper glance is formed. Cuprous oxide treated with hydrogen sulphide gives copper glance. According to Durocher, this is also obtained at a red heat from copper chloride.

Copper Pyrites.—The author obtained small crystals of copper pyrites by the action of hydrogen sulphide on a mixture of $2CuO + Fe_2O_3$, slightly heated in a glass tube. Copper pyrites is also formed by treating copper carbonate and ferric sulphate with sulphuretted hydrogen water in a closed tube for three days.

Bornite.—By the action of sulphuretted hydrogen on a mixture of Cu_2O, CuO, and Fe_2O_3, bornite is obtained at a low temperature, 100° to 200°. The compound $Cu_9Fe_4S_{10}$, which contains less copper and more iron than the normal bornite (CuS,Cu_2S,FeS), was obtained from a mixture of $2Fe_2O_3,3Cu_2O,3CuO$. In other experiments, a mixture rich in iron, $Cu_2S,2CuS,4FeS$, and a mixture rich in copper, were obtained. The experiments seem to prove that bornite differs from copper pyrites in requiring both CuS and Cu_2S. The ratio of the two to FeS is not absolutely fixed; and CuS and Cu_2S need not be present in equal quantities.

Bournonite is obtained by the action of hydrogen sulphide on the corresponding chlorine and oxygen compounds of lead, copper, and antimony, at a low heat.

Miargyrite was obtained by heating a mixture of antimony and silver chlorides, corresponding with the proportion Ag : Sb = 1 : 1, in a glass tube through which a strong stream of hydrogen sulphide passed.

Jamesonite was obtained by the action of hydrogen sulphide on a mixture of antimony or antimony oxide and lead chloride at a temperature of 200° to 400°. B. H. B.

Massive Safflorite. By L. W. McCay (*Amer. J. Sci.*, **29**, 369—374).—In a previous paper (Abstr., 1884, 1098) the author showed that the rhombic modification of speiskobalt, described by Sandberger as spathiopyrite, is identical with the safflorite of Breithaupt. Sandberger (Abstr., 1884, 405), admitting the existence of the crystalline safflorite, objected to the use of the term to cover the massive varieties, and doubted the accuracy of the statement that speiskobalt and safflorite appear together, the former above the latter. The author has therefore examined some specimens of speiskobalt from the Freiberg collection, exhibiting the occurrence of smaltine and massive safflorite together. An analysis of a specimen of the grey cobalt arsenide, called by the Schneeberg miners *Schlackenkobalt*, gave the following results:—

As.	S.	Co.	Ni.	Fe.	Cu.	Bi.	Insoluble.	Total.
69·52	0·90	18·36	absent	9·40	0·62	trace	1·30	100·10

This analysis agrees in a curious way with v. Kobell's analysis of *Eisenkobaltkies* (safflorite) from Schneeberg; the quantity of cobalt shown in the author's analysis being identical with the quantity of iron in v. Kobell's, and *vice versâ*. The author is consequently inclined to believe that v. Kobell made a mistake in writing down his figures.

The specific gravity, 7·167, together with the results of the analysis, prove that the heavy grey Schlackenkobalt is massive safflorite, and the accompanying tin-white smaltine demonstrates conclusively that safflorite and smaltine occur together. B. H. B.

The Crystal Forms of the Andreasberg Calcite. By F. Sansoni (*Zeit. Kryst. Min.*, **10**, 545—600).—This paper, the first part of a monograph on calcite, treats of the crystal forms of the Andreasberg calcite. The author has examined 2500 specimens in various public and private collections, and has measured 722 crystals. He finds that the number of forms occurring on Andreasberg calcite amounts to 131, and that 359 combinations of these forms have, up to the present time, been met with. B. H. B.

Determination of the Refractive Indices of Boracite. By E. Mallard (*Zeit. Kryst. Min.*, **10**, 631—632).—For the determination of the refractive indices, the author employed the measurement of the relative retardation experienced by two principal vibrations running perpendicularly to a crystal plate; the measurements being made by means of a Babinet compensator. In sections of boracite parallel to the dodecahedron planes, the portions perpendicular to the negative

bisectrix gave $n_b - n_c = 0{\cdot}00597$. This observation combined with Des Cloizeaux's measurement of the axial angle V = 41° 47′ gives $n_b - n_a = 0{\cdot}00477$; from which is deduced $n_c - n_a = 0{\cdot}01074$. Combining these data with the mean refractive index ($n_b = 1{\cdot}667$) determined by Des Cloizeaux, the three principal indices are found to be: $n_a = 1{\cdot}6622$; $n_b = 1{\cdot}6670$; $n_c = 1{\cdot}6730$. B. H. B.

Formation of Beds of Sodium Nitrate. By A. Müntz (*Compt. rend.*, **101**, 1265—1267).—The author's previous observations and experiments (*Compt. rend.*, **85**, 1020; **100**, 1136; **101**, 65, 248, and 1136; see Abstr., 1884, *et seq.*), lead to the following conclusions. The nitric acid is derived from organic matter by oxidation under the influence of a nitrifying ferment; sea-water, or the mother-liquor of brackish marshes, has come in contact with the organic matter during nitrification; the sodium nitrate has been produced by the action of sodium chloride on the calcium nitrate originally formed; the sodium nitrate has not been formed in its present position, but has been removed from its place of origin, and afterwards concentrated in the beds in which it is now found. C. H. B.

Mimetesite, containing Lime, from Puy-de-Dôme. By A. Damour (*Zeit. Kryst. Min.*, **10**, 627).—Small botryoïdal masses of a greyish colour, from the Villevieille mine at Pontgibaut, gave on analysis—

As_2O_5.	P_2O_5.	PbO.	CaO.	Cl.	Pb.	Total.	Sp. gr.
19·65	3·44	63·25	3·46	2·57	7·49	99·86	6·65

This corresponds with the formula $(Pb,Ca)_5Cl[(As,P)O_4]_3$.
B. H. B.

Pectolite from Alaska. By H. Fischer (*Zeit. Kryst. Min.*, **10**, 614).—An analysis of pectolite from Port Barrow gave the following results:—

SiO_2.	CaO.	MgO.	Na_2O.	Al_2O_3.	H_2O.	Total.	Sp. gr.
53·94	32·21	1·43	8·57	0·58	4·09	100·82	2·873

Colour, pale apple-green; compact; easily fusible. B. H. B.

New Locality for Nephrite in Asia. By A. B. Meyer (*Zeit. Kryst. Min.*, **10**, 612).—A dark green mineral brought from Yunan by Anderson, is, according to Arzruni, typical nephrite. Analysis gave—

SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	H_2O.	Total.
56·58	0·92	4·12	12·92	21·65	3·25	99·44

The author suggests that Yunan or Barma is a hitherto unknown locality for Chinese nephrite. B. H. B.

Optical Properties of Albite. By A. Des Cloizeaux (*Zeit. Kryst. Min.*, **10**, 628—631).—Although albite has, of all felspars, the most constant composition, its optical properties vary according to

the homogeneity of the crystals, the number and disposition of the twin lamellæ and the manner of its occurrence. Regarding the properties of the crystals from the crystalline schists and in dolomitic limestones as normal, the following may be given :—The plane of the optic axes is always perpendicular to a plane which bevels the acute edge 0P, $\infty\bar{P}\infty$, and with 0P forms the angle S = 78° to 79°. Double refractive positive. The first bisectrix is almost perpendicular to the edge 0P, $\infty\bar{P}\infty$; $2H_a$ = 80° to 85° red; dispersion ρ less than v; $2H_o$ = 104° to 106°; plates perpendicular to the second bisectrix exhibit crossed dispersion with more or less distinct inclined dispersion. Normal results of this kind were given by transparent crystals from the Tyrol, Modane, Dauphiné, greyish-white crystals from Arendal, large white crystals from Karabinsk in the Ural, olafite from Snarum, small crystals from Calvados, red masses from Piedmont, white masses from the Mer de Glace at Chamouni, red masses from Mineral Hill, Pennsylvania, peristerite from Perth in Canada, yellow aggregates from Morongoze, and small white masses from S. Marcel and Piedmont.

Variations from the normal optical characters were shown by the following varieties of albite :—Moonstone from Mineral Hill, greyish-green masses from Moriah, New York, peristerite from Bathurst and Burgess in Canada, partly kaolinised masses from St. Vincenz in Styria, white aggregates from Hammerfest, pericline from the Tyrol, reddish-grey masses from Arendal; tschermakite from Bamle, Middletown in Connecticut, Irigny, Eureka in Victoria.

The position of the optic axes is uncertain in the varieties from Crique Boulanger in French Guiana, and from Miask.

B. H. B.

Andesine from Ardèche. By A. Damour (*Zeit. Kryst. Min.*, **10**, 646).—Small, transparent, colourless fragments, with distinct striation, from a volcanic tuff of the Coirons, near Rochesauve in the department of Ardèche, gave on analysis the following results :—

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	Total.	Sp. gr.
58·71	25·49	9·05	5·45	0·78	99·48	2·68

In the same tuff the following minerals were also found : octahedra of magnetite, yellow titanite, augite, and apatite. B. H. B.

Analysis of Labradorite from the Krakatoa Ashes. By A. Sauer (*Zeit. Kryst. Min.*, **11**, 59).—The results were as follows :—

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	Total.
51·03	28·37	10·74	8·74	1·11	99·99

B. H. B.

Analysis of Enstatite and Labradorite from the Enstatite-Porphyrite of the Cheviot Hills. By J. Petersen (*Zeit. Kryst. Min.*, **11**, 69—70).—The results of the analyses were as follows :—

	SiO_2.	Al_2O_3.	FeO.	MgO.	CaO.	H_2O.	K_2O.	Na_2O.	Total.
I.	52·53	3·38	9·89	26·66	6·19	0·26	—	—	98·91
II.	56·04	29·48	—	0·05	10·09	—	0·57	6·41	102·64

I, enstatite, sp. gr. 3·331; II, labradorite, sp. gr. 2·666.

B. H. B.

Analyses of Diallage, Labradorite, Aragonite, and Picrolite. By H. TRAUBE (*Zeit. Kryst. Min.*, **11**, 60—61).—Diallage (I), and labradorite (II), from the gabbro of the Buchberg, Lower Silesia, gave on analysis the following results :—

	SiO_2.	Al_2O_3.	FeO.	Fe_2O_3.	MnO.	CaO.	MgO.
I.	51·23	1·21	11·57	—	1·26	17·07	16·11
II.	52·08	27·56	—	1·65	—	12·23	0·60

	H_2O.	K_2O.	Na_2O.	Total.	Sp. gr.
I.	1·31	—	—	99·76	3·18
II.	—	4·82	0·80	99·74	2·71

Aragonite (III) from the magnesite of the Wachberg, near Baumgarten, Lower Silesia, and globular radiated aragonite (IV) with included magnesium carbonate, from the same locality, gave on analysis—

	CO_2.	CaO.	MgO.	Total.	Sp. gr.
III.	44·14	55·33	0·44	99·91	2·91
IV.	45·73	44·87	9·36	99·96	2·94

Picrolite from Endersdorf, Lower Silesia, gave—

	SiO_2.	FeO.	Al_2O_3.	MgO.	CaO.	H_2O.	Total.	Sp. gr.
V.	43·46	2·25	1·26	40·98	trace	12·25	100·20	2·65

corresponding with the formula $H_2Mg_3Si_2O_8 + H_2O$. B. H. B.

Hyalophane from Jakobsberg in Wermland, Sweden. By L. J. IGELSTRÖM (*Zeit. Kryst. Min.*, **10**, 632).—The author has analysed a greenish-blue compact felspar, which occurs with hausmannite and manganese-epidote in the limestone of the Jakobsberg mine. The results were as follows :—

SiO_2.	Al_2O_3.	BaO.	MgO.	MnO.	$K_2O + Na_2O$.	Total.
53·53	23·33	7·30	3·23	trace	11·71	99·10

B. H. B.

Analysis of Felspar, Augite, and Mica. By G. LINCK (*Zeit. Kryst. Min.*, **11**, 63—66).—Analyses of minerals from the minette of Weiler, near Weissenberg, gave the following results :—

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	K_2O.
I.	57·15	—	17·29	2·39	—	1·96	1·59	7·83
II.	48·23	—	5·28	4·83	5·01	15·84	19·85	0·52
III.	36·61	3·16	15·26	5·11	8·32	16·81	2·71	7·00

	Na_2O.	F.	H_2O.	Total.
I.	2·57	—	1·00	101·78
II.	0·67	—	0·45	100·68
III.	trace	0·20	4·95	100·13

I, felspar (sp. gr. 2·633); II, augite; III, mica. B. H. B.

Topaz from Stoneham, Maine. By F. W. Clarke and J. S. Diller (*Amer. J. Sci.*, **29**, 378—384).—C. M. Bradbury (Abstr., 1884, 27) published an analysis of the Stoneham topaz, showing it to be unlike any topaz hitherto known. The peculiar interest attaching to his results made a new analysis desirable. Some apparently altered topaz has now been found, the crystals of which, having the unchanged mineral at the centre, are transformed on the surface into a dark-purple soft substance. Between the purple zone and the topaz was a greenish intermediate layer. Damourite was intimately associated with the topaz in all the specimens examined. The results of the analyses may be tabulated as follows:—

I, unaltered topaz (sp. gr. 3·51, H. 8); II, greenish layer (sp. gr. 3·42, H. 7); III, purple zone (sp. gr. 2·82, H. 3); IV, massive damourite; V, foliated damourite:—

	I.	II.	III.	IV.	V.
SiO_2	31·92	35·15	44·52	45·19	45·34
Al_2O_3	57·38	53·18	46·19	33·32	33·96
F	16·99	12·88	0·40	—	—
H_2O	0·20	0·90	3·74	4·48	4·78
K_2O	0·15	1·52	2·30	11·06	10·73
Na_2O	1·33	1·28	2·82	1·57	1·49
FeO	—	—	—	4·25	3·96
MnO	—	—	0·21	0·58	0·51
CaO	—	1·32	0·30	trace	0·22
MgO	—	0·17	0·14	0·36	0·10
Totals	107·97	106·40	100·62	100·81	101·09
Deduct O	7·16	5·42	0·16		
Totals	100·81	100·98	100·46		

The topaz is thus ordinary topaz, with none of the anomalous character indicated by Bradbury. The analyses point to a progressive change from topaz to damourite, the fluorine and some alumina being gradually eliminated. This change was probably brought about by the kaolinisation of adjacent felspathic material.

The results of a crystallographic and microscopic examination were even more conclusive than the analyses in showing that the altered topaz is essentially damourite.

The fluorine washed out from the topaz in the form of alkaline fluorides, enters into new combinations, represented at the locality by fluorite, herderite, triplite, and apatite. B. H. B.

Rubellan. By M. U. Hollrung (*Zeit. Kryst. Min.*, **11**, 53).—The author has investigated the occurrence of rubellan in the basalt tuffs of Schima and Kostenblatt, in the nepheline dolerite of the Löban Mountain, and in the basalt lava of the Laacher See. He arrives at the conclusion that rubellan is not homogeneous, but is an alteration-product. He also states that two different minerals go by the name

of rubellan. He therefore proposes that the name rubellan should be omitted from the mica series.

Rubellan from three different specimens from the Laacher See gave on analysis the following results :—

	F.	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.
I*a*.	--	36·25	0·88	14·88	28·04	3·24	11·18
I*b*.	—	35·90	0·65	15·34	27·69	3·24	11·31
II*a*.	1·32	36·99	0·61	18·17	22·19	1·81	11·75
II*b*.	—	36·97	0·80	17·94	22·81	1·50	11·97
III*a*.	1·19	36·63	1·08	17·11	25·83	1·19	11·78
III*b*.	—	37·09	1·24	17·02	25·96	1·19	11·53

	K_2O.	Na_2O.	H_2O.	Total.
I*a*.	1·87	1·25	3·29	100·88
I*b*.	1·59	1·38	3·31	100·41
II*a*.	1·66	1·58	3·59	99·67
II*b*.	1·60	1·42	3·61	98·62
III*a*.	1·88	0·39	4·51	101·59
III*b*.	2·01	0·38	4·66	101·08

The sp. gr. of II was 2·81 to 2·86, and of III, 2·50. B. H. B.

Blue Tourmaline from Chapey. By A. Michel-Lévy (*Zeit. Kryst. Min.*, **10**, 649).—In the pegmatite veins in the gneiss of Chapey, near Marmagne (Saône-et-Loire), small strings of a blue substance occur, composed of minute fragments embedded in clay. This blue mineral is uniaxial, and gives a difference of the refractive indices $\omega - \gamma = 0{\cdot}0234$, a difference which corresponds with tourmaline only. This view is supported by the pleochroïsm and sp. gr. of the substance. B. H. B.

Analyses of Plagioclase and Olivine from Chili. By H. Ziegenspeck (*Zeit. Kryst. Min.*, **11**, 69).—Plagioclase (I) and olivine (II), from the basalt of the Volcano Yate, gave on analysis the following results :—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.
I.	46·03	32·41	1·78	—	13·78	0·28	0·75	4·43
II.	38·47	—	—	24·83	—	37·62	—	—

	Ignition.	Total.	Sp. gr.	
I.	0·48	99·94	2·74	
II.	—	100·92	3·48	B. H. B.

Artificial Preparation of Rhodonite. By L. Bourgeois (*Zeit. Kryst. Min.*, **10**, 626—627).—By fusing MnO_2 (1 mol.) and SiO_2 (1 mol.) for a short time, an aggregate of prisms of rhodonite is obtained. A mixture of MnO_2 (2 mols.) and SiO_2 (1 mol.) gives rhombic plates of tephroite, with small pyramids of hausmannite surrounded by a crystalline aggregate of rhodonite. An intermediate mixture of MnO_2 and SiO_2 gives a perfectly crystalline mass consisting

of large rhombic plates of tephroite, hausmannite, and rhodonite filling the space between the crystals. By employing $MnCl_2$, hausmannite and tephroite are obtained with very fine crystals of rhodonite 0·5 mm. long. These crystals have exactly the composition represented by the formula $MnSiO_3$. The planes observed and the optical properties are exactly the same as those of the natural crystals.

B. H. B.

Deposit from the Spring at Chabetout. By F. Thabuis (*Compt. rend.*, **101**, 1163—1164).—The spring at Chabetout, Puy-de-Dôme, issues from a compact rock formed of mica schist and gneiss, impregnated with crystals of iron pyrites, and containing traces of arsenical pyrites. The deposit from this water is ochreous and unctuous, and contains micaceous plates and golden-yellow plates. It has the following percentage composition after drying in the air:—

CaO.	MgO.	Alkalis.	Organic matter.	Sand, mica, &c.	H_2O.	CO_2.
2·234	0·276	0·406	9·400	2·087	22·900	1·820

As_2O_5.	P_2O_5.	SiO_2.	Fe_2O_3.	Mn_2O_3.	Al_2O_3.
0·230	0·145	11·137	49·410	0·305	0·900

The deposit contains lithium. The association of arsenic acid with phosphoric acid is unusual; the former exists as basic ferric arsenate, the latter as calcium phosphate.

C. H. B.

Organic Chemistry.

Physical Properties of Paraffins from Pennsylvanian Petroleum. By A. Bartoli and E. Stracciati (*Gazzetta*, **15**, 417—446.)—In this paper a number of determinations are given of the coefficients of expansion, capillarity and friction, the specific volumes and specific heats, indices of refraction and specific inductive powers of the paraffins from C_5H_{12} to $C_{16}H_{34}$, obtained from Pennsylvanian petroleum. These physical constants, with the exception of the specific volumes, increase regularly with increase of molecular weight; the specific heat is practically constant for all the hydrocarbons, and the specific inductive powers are in accordance with the laws of Maxwell.

V. H. V.

Normal and Primary Monochlorobutyl-derivatives. By L. Henry (*Compt. rend.*, **101**, 1158—1161).—The author has prepared a number of derivatives from chlorobromopropane, $CH_2Cl{\cdot}CH_2{\cdot}CH_2Br$, by taking advantage of the different reaction aptitudes of the groups CH_2Cl and CH_2Br. *γ-Chlorobutyronitrile*, $CH_2Cl.CH_2{\cdot}CH_2{\cdot}CN$, is a colourless, mobile liquid, with a faint disagreeable odour and a piquant taste. It is insoluble in water, but easily soluble in alcohol and in ether; it boils without decomposition at 195—197° under ordinary pressure; sp. gr. at 10° compared with water at the same

temperature = 1·1620. It dissolves in concentrated hydrochloric acid with slight development of heat, and if the solution is heated in sealed tubes, the corresponding acid is obtained. *γ-Chlorobutyric acid*, $CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is a thick, viscous, colourless liquid, with a feeble butyric odour and a burning taste; sp. gr. at 10° = 1·2498. It is feebly corrosive, and is only slightly soluble in water, but dissolves easily in alcohol and ether. When cooled in a mixture of sodium sulphate and hydrochloric acid, it crystallises in large, thin, perfectly transparent lamellæ, which melt and resolidify at 10—10·5°. γ-Chlorobutyric acid does not distil without decomposition under ordinary pressure; hydrochloric acid is given off abundantly at 180—185°, and at 200° butyrolactone, $<\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CO\end{matrix}>O$, distils over. This is a very convenient method of preparing butyrolactone; the product boils at 200—201°; sp. gr. at 10° = 1·1295.

The methyl and ethyl salts of γ-chlorobutyric acid were prepared by dissolving the nitrile in the respective alcohols, saturating the solution with hydrochloric acid, and heating for some time. They are colourless liquids, with an agreeable odour somewhat resembling that of menthol, and a sharp piquant taste. They are insoluble in water, and react very slowly with aqueous ammonia at the ordinary temperature. *Methyl γ-chlorobutyrate* boils at 173—174° under a pressure of 758 mm.; sp. gr. at 10° = 1·1894. *Ethyl γ-chlorobutyrate* boils at 183—184° under the same pressure; sp. gr. at 10° = 1·1221. *Normal primary chlorobutyric chloride*, $CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}COCl$, easily obtained by the action of phosphorus trichloride on the acid, is a colourless liquid with a disagreeable, suffocating odour; sp. gr. at 10° = 1·2679. It boils at 173—174° under a pressure of 750 mm., that is, at practically the same temperature as methyl γ-chlorobutyrate, and in this respect it follows the law which connects the boiling points of the methyl salts and of the acid chlorides in the butyric series. γ-Chlorobutyric chloride has the general properties of the acid chlorides. *γ-Chlorobutyramide*, $CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}CONH_2$, obtained by the action of ammonia on the methyl salt or the acid chloride, is a solid compound, which melts at 88—90°, and cannot be distilled. It is only slightly soluble in water, but dissolves easily in hot alcohol, from which it crystallises in needles. C. H. B.

Constitution of Cyanuric Acid. By J. Ponomareff (*Ber.*, **18**, 3261—3275; compare Abstr., 1882, 937).—A polymeride of cyanogen bromide, $C_3N_3Br_3$, is obtained by the action of dry hydrogen bromide on cyanogen bromide dissolved in absolute ether. It resembles solid cyanogen chloride in its properties. When heated at 140—150° with acetic anhydride, it decomposes into cyanuric acid and acetic bromide. Sodium ethoxide and methoxide act on it readily, with formation of normal ethyl and methyl cyanurate respectively.

Phosphorus pentachloride acts on ethyl cyanurate in the same way as on the methyl salt, with formation of solid cyanogen chloride. Ammonia at 170—180° converts ethyl cyanurate into melamine and ammeline.

Diethylcyanuric acid, $C_3N_3(OEt)_2{\cdot}OH$, isomeric with Limpricht and

Habich's diethylcyanuric acid, is obtained by the action of baryta on normal ethyl cyanurate. It forms a crystalline powder, sparingly soluble in alcohol and cold water. The *barium salt* (with 3 mols. H_2O) crystallises in plates; it separates from a dilute aqueous solution in small needles with 12 mols H_2O. The *lead* and *silver salts* were prepared. Ethyl iodide acts on the lead salt with formation of normal ethyl cyanurate.

When potassium ethyl sulphate is heated with sodium cyanurate at 160°, ethyl isocyanurate is formed (compare this vol., p. 42). Ethyl iodide acts on mono- and di-potassium cyanurate with formation of diethyl cyanurate melting at 173°, identical with Limpricht's compound (*Annalen*, **109**, 112). By the action of methyl iodide on silver cyanurate at 100°, methyl isocyanurate, and a small quantity of normal methyl cyanurate, were obtained. In presence of an excess of the iodide, the reaction takes place at the ordinary temperature; the yield of normal cyanurate is then much larger.

Acetic chloride acts on silver cyanurate with rise of temperature and formation of acetic anhydride and *triacetyl cyanurate*, $C_3N_3O_3Ac_3$. This compound melts at 170° with partial decomposition; it is insoluble in ether, sparingly soluble in chloroform. When warmed with water, it decomposes into acetic and cyanuric acids.

These results show that cyanuric acid belongs to the same series as the normal and alkyl salts of cyanuric acid; that is to say, it contains three hydroxyl-groups united with the group C_3N_3. N. H. M.

Additive Products of Cyanogen Compounds: Constitution of Dicyandiamide and Melamine. By B. Rathke (*Ber.*, **18**, 3102—3112). — Dicyandiamide reacts readily with thiocyanic acid with formation of thioammeline. On the assumption that dicyandiamine has the constitution $NH_2{\cdot}C(NH){\cdot}NH{\cdot}CN$ (compare Bamberger, Abstr., 1883, 1090), the author ascribes to thioammeline the formula $NH<\begin{matrix}C(NH){\cdot}NH\\C(NH){\cdot}NH\end{matrix}>CS$. Melanurenic acid, obtained by the action of carbonic anhydride on dicyandiamide, would have an analogous constitution. This is contrary to the opinion expressed by Hofmann (this vol., p. 41). The author does not think, however, that it will be possible to find single formulæ which will account for all reactions of these compounds, and recommends the use of Hofmann's formulæ (*loc. cit.*) together with his own. N. H. M.

Preparation of Alkyl Bisulphides. By E. Courant and V v. Richter (*Ber.*, **18**, 3178—3180).—It was thought probable that the action of sulphuryl chloride on mercaptan might lead to the formation of ethyl dithiosulphate, $SO_2(SEt)_2$, but the reaction takes a different course and yields ethyl bisulphide. This gives a better method for the formation of the bisulphides than those previously employed. A. J. G.

Ethereal Salts of Nitrous Acid. By G. Bertoni (*Gazzetta*, **15**, 351—360 and 361—370).—*Ethylene Nitrite*, $ON{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}NO$.—The compound of the empirical formula $C_2H_4N_2O_4$, first prepared by

Semenow (*Zeit. Chem.*, 1864, 129), is regarded by some as nitroethylene, by others as the ethylene salt of nitrous acid. The latter view is, however, incorrect, as the true ethereal salt, prepared by the general process previously described by the author, differs from Semenow's compound. The process consists in distilling glyceryl trinitrite with ethylene glycol, the compound passing over at 90—105°; it is redistilled in a current of carbonic anhydride.

It is a mobile, yellow liquid, boiling at 96—98°, sp. gr. at 0° = 1·2156, insoluble in water, soluble in methyl and ethyl alcohols, ether, chloroform, and glycerol. When inspired, it produces vertigo and paralysis of the respiratory system. On exposure to air, it is gradually converted into oxalic acid. It gives a violet coloration with concentrated sulphuric acid, and, when distilled with methyl alcohol, it is converted into ethylene glycol and methyl nitrite.

Tertiary butyl nitrite, $C_4H_9{\cdot}O{\cdot}NO$, is prepared in a manner similar to the ethylene compound, from tertiary butyl alcohol and glyceryl trinitrite. It is a yellow, mobile liquid, boiling at 63°, sp. gr. at 0° = 0·8914, sparingly soluble in water, soluble in alcohol, ether, and chloroform. It is rapidly decomposed by acids with evolution of nitrous fumes.

The tertiary butyl nitrite obtained with its isomeric nitro-compound, described by Tschermak as boiling at 67—68°, was probably contaminated with its isomeride.

Allyl Nitrite, $C_3H_5{\cdot}O{\cdot}NO$.—Prepared as above from equimolecular proportions of glyceryl trinitrite and allyl alcohol, the two liquids being mixed in a vessel kept cool; the mixture is then quickly distilled, the portions passing over at 50° being retained. This fraction is then dried over lime and distilled in a water-bath below 100°, inasmuch as at this temperature it is completely decomposed with explosive violence. It is a mobile liquid boiling at 44°; sp. gr. at 0° = 0·9546, insoluble in water, soluble in methyl alcohol, and decomposing into methyl nitrite and allyl alcohol. It is rapidly decomposed by mineral acids, and when heated it evolves nitrous fumes, and acraldehyde is formed. On prolonged contact with water, it is slowly destroyed, forming a white crystalline mass which is rapidly resinified.

V. H. V.

δ-Hexyleneglycol and its Oxide. By A. Lipp (*Ber.*, **18**, 3275—3286).—*Ethylic bromopropylacetoacetate*,

$$CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}CHAc{\cdot}COOEt,$$

is prepared by adding a solution of 6 grams of sodium in 60 grams of absolute alcohol to 32 grams ethyl acetoacetate; the product is then added to 80 grams trimethylene bromide. The alcohol is distilled off, the residue treated with water and shaken with dilute potash (to dissolve out unchanged ethyl acetoacetate), and then dried. It is insoluble in water, but soluble in alcohol. When boiled with 5 per cent. hydrochloric acid, it decomposes into bromobutyl methyl ketone, alcohol, and carbonic anhydride. Alcoholic ammonia converts it into ethylic trimethyleneacetoacetate (*Ber.*, **16**, 208).

Normal acetobutyl alcoholic, $COMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, is obtained by boiling 50 grams of ethyl bromopropylacetoacetate with 50 grams

of water and 20 grams of hydrochloric acid (sp. gr. = 1·1) until the evolution of carbonic anhydride ceases. When cold, the solution is separated from an oil (consisting of bromine compounds), partially distilled, and then supersaturated with potassium carbonate. The acetobutyl alcohol separates as an oil, and is dried with potassium carbonate and over sulphuric acid to remove ethyl alcohol. It is very readily soluble in water, alcohol, and ether; it boils at 154—155° under 718 mm. pressure, with slight decomposition; sp. gr. = 1·0143 at 0°. It has an odour resembling that of camphor. Sulphuric acid and potassium dichromate oxidise it to acetobutyric acid.

Bromobutyl methyl ketone, $COMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$, is obtained by distilling acetobutyl alcohol with five times the amount of strong hydrobromic acid. It is a colourless oil, of agreeable odour, sparingly soluble in water, readily in alcohol and ether. It boils at 214—216° (under 718 mm. pressure). Alcoholic ammonia acts on it with formation of ammonium bromide and a base having the odour of piperidine.

δ-Hexylene glycol, $OH{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2OH$, is formed by the action of sodium amalgam on acetobutyl alcohol. It is a thick colourless liquid, readily soluble in alcohol, less soluble in ether. It boils at 234—235° under 710 mm. pressure, sp. gr. at 0° = 0·9809. When heated with fuming hydrochloric acid at 100°, it is converted into the corresponding monochlorhydrin. This is almost insoluble in water, and has an agreeable odour.

δ-Hexylene oxide, $<\begin{matrix}CH_2{\cdot}CH_2{\cdot}CH_2\\CH_2—CHMe\end{matrix}>O$, is prepared by heating 10 grams of δ-hexylene glycol with 20 grams of sulphuric acid and 10 grams of water for one hour at 100°. The product is diluted with water and distilled; the distillate is then dried by means of potassium carbonate and redistilled. It is a colourless liquid having a strong odour, resembling, when dilute, that of ethyl ether. It boils at 103—104° (under 720 mm. pressure). It is sparingly soluble in water, readily in ether and alcohol. Water at 225—230° and ammonia at 200° have no action on it. Hydrochloric acid (sp. gr. 1·1) at 100° converts it into the *monochlorhydrin*, $CHMeCl{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, mentioned above; prolonged heating with fuming hydrochloric acid converts it into hexylene dichloride, which can also be obtained from the glycol. The low boiling point of δ-hexylene oxide and its behaviour towards dilute hydrochloric acid, support the constitutional formula ascribed to it. The elimination of water from δ-hexylene glycol does not therefore take place in the same way as in the case of the α-glycols, which yield unsaturated alcohols. N. H. M.

Cyanhydrin of Levulose. By H. Kiliani (*Ber.*, **18**, 3066—3072).—Levulose was prepared by boiling 50 grams of inulin with 150 grams of water and 10 c.c. of dilute sulphuric acid for eight hours. The acid was then precipitated by baryta, the filtrate evaporated and mixed with 5—6 vols. of alcohol. In 24 hours, a voluminous, brown substance separated. The filtrate was evaporated to a syrup, and then shaken up with strong hydrocyanic acid which converted the levulose into the *cyanhydrin*, $C_7H_{13}O_6N$. This is readily

soluble in water, insoluble in alcohol and ether. When heated, it softens between 100—105°, and becomes strongly coloured. Fuming hydrochloric acid converts it at the ordinary temperature into an acid which could only be obtained as a syrup. This when boiled with concentrated hydriodic acid and amorphous phosphorus yields a *heptolactone*, $C_7H_{12}O_2$, which boils at 220°; it does not solidify in a freezing mixture. When the lactone is heated with hydriodic acid and amorphous phosphorus at 180°, it yields an acid boiling at 209·6° which could not be got to solidify, and therefore is not normal heptylic acid. The *calcium salt* (with 5—6 mols. H_2O) crystallises in long needles. The results do not agree with the description of calcium methybutylacetate given by Hecht, and the acid is probably ethylpropylacetic acid. The formation of this acid would point to the constitution $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}CO{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$ for levulose.

N. H. M.

The Succession of the Rate of Retrogressive Birotation of some Saccharoses and Glucoses with regard to their Constitutional Formulæ and the Extent of Affinity. By F. Urech (*Ber.*, **18**, 3047—3060).—Milk-sugar is not changed by oxalic acid. When 9·34 grams of milk-sugar are dissolved in 11·83 grams hydrochloric acid and kept for 28 days at 10°, the milk-sugar was recovered unchanged. Saccharose, under the same conditions, is completely inverted in nine hours. When three times the quantity of hydrochloric acid is used, the milk-sugar is slowly inverted. According to Meissl, maltose occupies a position between that of milk-sugar and saccharose with regard to its invertibility. Solutions of alkalis act more quickly on maltose than on milk-sugar, and more quickly on milk-sugar than on saccharose. This indifferent behaviour of saccharose may be accounted for by assuming that the relations of the glucose radicles to one another are different in saccharose; for instance, that the glucoses are joined by an oxygen-atom to form an ether.

Alkali solutions act on lactose more slowly than on dextrose, and on dextrose more slowly than on levulose; a table with the results of experiments is given (compare Abstr., 1884, 1112).

The author has already (*loc. cit.*) shown that dextrose reduces alkaline copper solution more slowly than levulose; further experiments show that the action of lactose is still slower. Fehling's solution decomposes maltose more quickly than milk-sugar; saccharose is decomposed slowly at a higher temperature.

The results of comparative experiments made with lactose and dextrose show that the retrogressive birotation of the latter takes place rather more quickly than in the case of lactose. N. H. M.

Composition and Properties of Raffinose. By H. Pellet and L. Biard (*Chem. Centr.*, 1885, **47**, 878—879).—The authors confirm Loiseau's investigations. A crystalline raffinose containing 15·1 per cent. of water was obtained. The rotatory power of inverted raffinose was found to be +66·7 (sugar = 100). Scheibler gives it as +67·1. It remains to be decided whether raffinose exists ready-formed in beetroot, or is formed during the treatment of the sap. From the action of acetic acid on raffinose, and from other considerations, the

authors conclude it to be a compound of crystallisable sugar with dextrin or some similar substance, and a certain amount of water.

H. P. W.

Source of Raffinose (Melitose) in the Products of the Manufacture of Sugar. By E. O. v. Lippmann (*Ber.*, **18**, 3087—3090).—Raffinose was obtained directly from beetroot sap by the method employed by Scheibler for the separation of raffinose from molasses (Abstr., 1885, 962). The presence of raffinose partly accounts for the high polarisation of beetroot sap.

The author does not hold Degener's view that the formation of dextrorotatory sugar in beetroot beginning to decompose is due to the action of maltose—especially as it has not been shown that the latter exists in the sap of beetroot.

N. H. M.

Researches on Rice-starch. By L. Sostegni (*Gazzetta*, **15**, 376—384).—On account of the discordant observations as to the amount of dextrose obtained from starch by the action of acids on it, this point is examined in the case of pure specimens of rice-starch. The ratio between the quantities of starch and dextrose was found to be 93·2 : 100, a result in accordance with the recent researches of Salomon (*J. pr. Chem.*, **25**, 348, and **26**, 342). In order to trace out the cause of the discrepancies, the author has examined the insoluble residue obtained in the course of the degradation of the starch molecule by unorganised ferments or by 1 per cent. hydrochloric acid. Ether extracted from the product a mixture of fatty acids, containing a proportion of carbon less than that required for palmitic or oleic acid. The ratio between the amido-cellulose, thus purified, and the dextrose obtained was found to be as 98·7 : 100, a result which is still low owing to the formation of other products of decomposition by the action of the acid used.

V. H. V.

Maltodextrin. By A. Herzfeld (*Ber.*, **18**, 3469—3470).—This paper contains a short explanation of a few points of difference between the observations of Brown and Morris on maltodextrin (Trans., 1885, 560) and those of the author (Abstr., 1880, 866). The former state that this compound does not undergo fermentation by *Saccharomyces cerevisiæ* of the high fermentation type until it is further hydrated, whereas the author found that it is readily and completely fermented by pressed yeast. This discrepancy arises from the difference of species of yeast used. Indeed, Brown and Morris themselves show that maltodextrin is fermented by the slow action of certain forms of saccharomyces such as *S. ellipticus* and *S. pastorianus* of the bottom fermentation type (comp. *supra*, 570). The author also allows that his former specimens of maltodextrin were not altogether free from maltose, and on a recent repetition of his work he is able to confirm Brown and Morris' data as to the composition and specific rotatory power of their maltodextrin.

V. H. V.

Action of Chlorine on Anhydrous Chloral. By H. Gautier (*Compt. rend.*, **101**, 1161—1162).—Sixty grams of chloral was placed in a flask of 10 litres capacity, which was then filled with chlorine

gas. No change takes place in the dark even after 15 days, but in diffused light a reaction proceeds slowly, and in direct sunlight the colour of the chlorine completely disappears in two or three hours. The products are hydrogen chloride, carbonic chloride, and carbon tetrachloride; the reaction being represented by the equation

$$CCl_3{\cdot}COH + 2Cl_2 = CCl_4 + COCl_2 + HCl$$

(comp. Beilstein, *Handbuch*, p. 760). C. H. B.

Preparation of Trichloracetic Acid. By A. Clermont (*Ann. Chim. Phys.* [6], **6**, 135—139).—One equivalent of chloral hydrate is melted at 50—55°, one equivalent of fuming nitric acid added, and the source of heat then removed; in a few minutes nitrous vapours are given off; the action ceases almost entirely in an hour's time. The liquid is then heated in a tubulated retort at 123° to 195°, whereby the whole of the nitric acid is removed; above 195° trichloracetic acid distils as a colourless liquid which solidifies on cooling. Trichloracetic acid exists in a state of superfusion at 52·2°, its normal point of solidification being 55·0°. Acetic acid may be readily reproduced from trichloracetic acid by heating equal volumes of saturated aqueous solutions of trichloracetic and fuming hydriodic acids in a sealed tube at 100° for 12 hours, the resulting liquid is exactly neutralised with potash, evaporated to dryness and the solid mass heated sufficiently to decompose any trichloracetic acid present; the potassium acetate may then be extracted with absolute alcohol. A. P.

Action of Nitrous Acid on Sulphonediacetic Acid. By J. M. Lovén (*Ber.*, **18**, 3241—3242).—When 1 mol. sulphonediacetic acid (Abstr., 1885, 241) is gradually added to a well-cooled, moderately concentrated solution of 2 mols. sodium nitrite, gas consisting mainly of carbonic anhydride is evolved, and the solution is found to contain sulphuric acid and a considerable amount of hydrocyanic acid. This reaction may be explained on the assumption that primary diisonitrososulphonediacetic acid is first formed, and that this simultaneously decomposes into carbonic anhydride, sulphuric and hydrocyanic acids. Higher homologues of sulphonediacetic acid would yield nitriles or products of their decomposition, in addition to carbonic anhydride and sulphuric acid. N. H. M.

Action of Acid Chlorides on Inorganic Compounds. By B. Lachowicz (*Ber.*, **18**, 2990—2996; comp. Abstr., 1884, 990).—Propionic and succinic chlorides act on dry lead nitrate with slight rise of temperature, and formation of propionic and succinic anhydrides respectively, nitrogen peroxide and oxygen being evolved. Analogous reactions take place between the chlorides of organic acids and all normal anhydrous nitrates of heavy metals. All metallic carbonates appear to react with the acid chlorides, with evolution of carbonic anhydride and formation of a salt of the organic acid; a trace of the anhydride is also formed. With the oxides of heavy metals, the reaction is much more vigorous; the chief product is the salt of the organic acid (comp. Abstr., 1878, 108). N. H. M.

Fat of the Fruit of Vateria Indica. By F. v. Höhnel and J. F. Wolfbauer (*Chem. Centr.*, 1885, 762)—There have lately been brought into commerce, under the name of butter beans, some peculiar fatty seeds, which are now identified as those of *Vateria indica*, a tree from which considerable quantities of vegetable tallow (Piney tallow, Malabar tallow) is derived. The air-dried seeds contain 49·2 per cent. of a greenish-yellow, solid fat, which bleaches rapidly on exposure to light, and has a peculiar, agreeable, balsamic odour. The fat is readily saponified, and yields a mixture of fatty acids melting at 56·6° and resolidifying at 54·8°. This mixture consists of oleic acid with solid fatty acids which melt at 63·8° and constitute about 60 per cent. of the vegetable tallow. A. J. G.

Synthesis of Ethyl Acetoacetate and Phloroglucinol. By A. Baeyer (*Ber.*, **18**, 3454—3460).—As a preliminary point, the author reopens the discussion between Frankland, Duppa, and Wislicenus on the one hand, and Geuther on the other, regarding the constitution of ethylic sodacetoacetate, namely, whether the sodium is combined directly with the carbon or indirectly by means of the oxygen. Against the latter view is the ready replacement of the metal by other groupings, which are then undoubtedly directly associated with the carbon. *Secondly*, there arises the difficulty of representing the constitution of ethylic sodomalonate, whereby it would be necessary to assume that the stable COOEt grouping undergoes an extraordinary transformation, leading to the production of a compound of formula $COOEt{\cdot}CH : C(ONa){\cdot}OEt$. *Thirdly*, the analogy drawn by Geuther as to the formation of ethylic sodacetoacetate with that of pinacone from acetone by the action of sodium through the intervention of a compound, $ONa{\cdot}CMe_2{\cdot}CMe_2{\cdot}ONa$, fails, inasmuch as it has been observed that whereas sodium has no action on ethyl succinate, yet sodium ethylate, free from alcohol, converts it readily into ethyl succinosuccinate. Further, the observations of Purdie on the action of sodium ethoxide on ethyl fumarate are rationally explained by the intermediate formation of ethylic sodethoxysuccinate, and its subsequent decomposition in the presence of alcohol with re-formation of sodium ethoxide and production of ethyl ethoxysuccinate (Trans., 1881, 344; 1885, 855); such an explanation is in complete accordance with the commonly received view of the constitution of ethylic sodacetoacetate. On applying these facts to the initial action of sodium on ethyl acetate, it follows that the original hypothesis of Frankland and Duppa regarding the intermediate formation of a compound, ethylic sodacetate, $CH_2Na{\cdot}COOEt$, is possibly correct. By the action of 1 atom of sodium on 2 mols. of ethyl malonate at a temperature of 110°, a substance of the composition $C_{15}H_{18}O_9$ is obtained, crystallising in needles which melt at 104°. It is insoluble in water, sparingly soluble in alcohol, readily soluble in ether and chloroform with pale-green fluorescence. It is analogous in its reactions to ethyl succinosuccinate, yet is much more stable; its constitution is thus probably similar, and it is doubtless derived from 3 mols. of ethyl malonate, the carbon-atoms being associated in a ring formula. It may thus be regarded as *methyl phloroglucinoltri-*

carboxylate, $C_6(OH)_3(COOEt)_3$, and this hypothesis is supported by the formation of phloroglucinol from it by fusion with potash.

Incidentally this synthesis of phloroglucinol raises the question whether its composition is correctly represented by its generally received formula, and not by the formula $CO<\begin{matrix}CH_2\cdot CO\\CH_2\cdot CO\end{matrix}>CH_2$; in support of the latter it is mentioned that hydroxylamine reacts with phloroglucinol to form a crystalline compound melting at 128°. It is proposed to make this point a subject of further investigation.

V. H. V.

Ethenylglycollic Acid. By C. A. Lobry de Bruyn (*Rec. Trav. Chim.*, **4**, 221—235).—Acraldehyde combines directly with hydrocyanic acid to form the nitrile of ethenylglycollic acid, which distils at 110° under a pressure of 85 mm.; sp. gr. at 15° = 1·05; it is soluble in alcohol and ether, but its preparation in a state of purity presents considerable difficulty. On saponification with hydrochloric acid, the nitrile is converted into *ethenylglycollic acid*,

$$CH_2:CH\cdot CH(OH)\cdot COOH,$$

which may be purified by means of its zinc salt. The acid is a syrupy liquid, solidifiying in a vacuum after some time, forming a crystalline mass of the consistency of camphor. Its *zinc* salt crystallises with $3H_2O$, its *potassium* salt is a gummy hygroscopic mass, and the *copper* salt a greenish-blue, indistinctly crystalline powder, very soluble in water, sparingly soluble in alcohol. The acid, as also its salts, readily take up bromine, a molecule of the acid combining with a molecule of bromine; but the acid, so far as it was examined, was probably not a dibromerythic acid.

V. H. V.

Pyrogenic Decomposition of Organic Acids. By Hanriot (*Compt. rend.*, **101**, 1156—1158).—The acids were distilled in contact with a large excess of quicklime.

Succinic acid yields ethane, $C_4H_6O_4 = 2CO_2 + C_2H_6$.

Adipic acid yields butane, $C_6H_{10}O_4 = 2CO_2 + C_4H_{10}$.

Glycollic acid under these conditions decomposes only at a red heat, and yields methane (2 vols.) and hydrogen (1 vol.), and small quantities of liquid products which are free from methyl alcohol. The decomposition seems to be very complicated.

Lactic acid yields alcohol, $C_3H_6O_3 = CO_2 + C_2H_6O$. This reaction renders it possible to pass from glucose to alcohol without the intervention of an alcoholic ferment.

Pyruvic acid yields only a very small quantity of aldehyde, the remainder being in all probability decomposed in contact with the lime.

C. H. B.

Vinaconic Acid. By R. Fittig and R. Marburg (*Ber.*, **18**, 3413—3414).—In this notice it is stated that Perkin's observation that vinaconic acid (trimethylenedicarboxylic acid) does not combine with bromine is incorrect, inasmuch as in chloroform solution in diffused daylight, it yields a dibromo-additive product,

$C_3H_4Br_2(COOH)_2$, in well-defined crystals, which melt at 100—110° with incipient decomposition. V. H. V.

Pentamethylenedicarboxylic Acid (1, 2). By W. H. PERKIN, Jun. (*Ber.*, **18**, 3246—3252).—*Ethyl pentanetetracarboxylate*,

$$CH(COOEt)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOEt)_2,$$

is prepared by gradually adding a mixture of 150 grams of ethyl malonate and 76 grams of trimethylene bromide to a cooled solution of 22 grams of sodium in 250 grams of absolute alcohol. In about an hour water is added, and the whole extracted with ether. On distilling off the ether, an oil is obtained which is distilled with steam, and fractioned under diminished pressure. The pure ether forms a very thick colourless oil, boiling at 259—262° (under 100 mm. pressure). When saponified, it yields a brown oily acid (probably *pentanetetracarboxylic acid*); this when heated gives off carbonic anhydride and yields α-pimelic acid.

By treating an ethereal solution of pentanetetracarboxylic acid (1 mol.) with sodium ethoxide (2 mols.), a *sodium compound*, $C_{17}H_{26}O_8Na_2$, is formed; and this when treated with bromine and subsequently saponified with alcoholic potash, yields *pentamethylenetetracarboxylic acid.* When this is heated at 200—220°, it decomposes into carbonic anhydride and *pentamethylenedicarboxylic acid.* This acid, $CH_2\begin{<}{CH_2{\cdot}CH{\cdot}COOH \atop CH_2{\cdot}CH{\cdot}COOH}$, crystallises in nodular masses which melt at 159—160°; it is readily soluble in hot water, alcohol, and ethyl acetate, sparingly in ether, benzene, chloroform, and light petroleum. The *silver salt* forms a sparingly soluble white precipitate. When the acid is heated for a long time at 300°, it gives off water, and yields the *anhydride* $CH_2\begin{<}{CH_2{\cdot}CH{\cdot}CO \atop CH_2{\cdot}CH{\cdot}CO}\!>\!O$. The latter compound melts at 64—67°, is readily soluble in ether, benzene, chloroform, and alcohol, more sparingly in light petroleum, and is almost insoluble in carbon bisulphide; if it is warmed with resorcinol and sulphuric acid, and ammonia is subsequently added, it gives the fluorescein reaction very splendidly. N. H. M.

Constitution of Carbopyrotritartaric Acid. By R. FITTIG (*Ber.*, **18**, 3410—3413).—In a former paper, the author has shown that ethyl acetoacetate reacts with succinic acid to form an acid isomeric with carbopyrotritartaric acid (this vol., p. 47); it is proposed to name it *methronic acid.* When heated at 200—240°, it is decomposed into carbonic anhydride and pyrotritartaric acid. Regarding the constitution of carbopyrotritartaric acid, the author regards its formation from diacetosuccinic acid as analogous to that of mesityl oxide from acetone, thus giving the formula—

$$CO\begin{<}{-CH:CMe- \atop CH(COOH)}\!>\!CH{\cdot}COOH.$$

On comparison with the formula of methronic acid,

$$CO<\begin{matrix}C(COOH):CMe\\CH_2\cdot CH(COOH)\end{matrix}>,$$

it is seen that both are α-β-dicarboxylic acids, in which the carboxylic groupings are in relatively different positions, but both acids would yield carbopyrotritartaric acid. V. H. V.

Action of Phosphoric Chloride on Alloxan. By G. Ciamician and P. Magnaghi (*Ber.*, **18**, 3444—3446).—As a continuation of observations on the action of phosphorus pentachloride on dichloromaleïmide (Abstr., 1884, 1116), the authors have examined the action of the same reagent on alloxan. On heating together alloxan, phosphoric chloride (24 parts), and phosphorus oxychloride (24 parts) at 126—136°, *tetrachloropyrimidine*, $C_4N_2Cl_4$, is formed. This substance crystallises in micaceous leaflets melting at 67—68°, and possessing a penetrating odour resembling that of camphor.

V. H. V.

Thiohydantoïn and its Derivatives. By R. Andreasch (*Monatsh. Chem.*, **6**, 821—843). — By digesting the nitrosothiohydantoïn obtained by Maly (Abstr., 1879, 712) with dilute hydrochloric acid in a sealed tube at 115—120°, it is completely decomposed, hydroxylamine occurring amongst the products of the reaction. It is probable, therefore, that this compound, as also the nitrosothioglycollic acid derived from it, are true isonitroso-compounds, a view which is supported by the fact that neither substance yields Lieberman's reaction with phenol and sulphuric acid. By the reduction of isonitrosothiohydantoïn with tin and hydrochloric acid, or with hydriodic acid, thiocarbamide and glycocine are formed together with a small quantity of a substance which is separated by means of ether; this forms a red powder, is soluble in water or alcohol with a brilliant yellow coloration and has an acid reaction; on the addition of alkalis it acquires a purple-red colour, which on acidifying again changes to yellow. Isonitrosothioglycollic acid when reduced by hydriodic acid yields glycocine alone, sulphur being precipitated.

Imidocarbamine-β-thiolactic acid, $NH_2\cdot C(NH)\cdot S\cdot CH_2\cdot CH_2\cdot COOH$, is formed by the action of carbamide on a concentrated aqueous solution of β-iodopropionic acid, and not, as was expected, the corresponding thiohydantoïn. This acid crystallises in needles and melts at 175—176° with decomposition; when digested with aqueous baryta, dithiolactic acid and β-thiolactic acid are formed. When a solution of the latter is mixed with dilute ferric chloride and an alkali is added, a brownish-red coloration is produced, which becomes more intense on shaking with air, but disappears on standing. By oxidising imidocarbamine-β-thiolactic acid dissolved in strong hydrochloric acid with potassium chlorate at 50—60°, carbamide, and β-sulphopropionic acid,

$$HSO_3\cdot CH_2\cdot CH_2\cdot COOH,$$

are obtained. The latter forms a strongly acid, colourless syrup. The silver salt forms small scales and is anhydrous; the barium salt,

$C_3H_4BaSO_5 + 5H_2O$, is soluble in water and has a neutral reaction. This acid is also formed when bromine is added to an aqueous solution of imidocarbamine-β-thiolactic acid.

Methylthiohydantoïn, $CO<^{CH_2\cdot S}_{-NMe-}>C:NH$, may be prepared by heating methyl thiocarbamide with chloracetic acid at 100°; it forms almost colourless crystals identical in appearance with thiohydantoïn, but differs from this compound in being soluble in ether and alcohol. By the action of nitrous acid, it is converted into *isonitrosomethylthiohydantoïn*, $C_4H_5N_3SO_2$; this forms a reddish powder, which is insoluble in ether, but dissolves in alcohol and hot water; it dissolves readily in aqueous alkalis, and on heating with aqueous baryta is converted into the barium salt of isonitrosomethylthioglycollic acid. A. P.

Constitutional Formula of Thiophen. By L. Gattermann, A. Kaiser, and V. Meyer (*Ber.*, **18**, 3005—3012).—The results of experiments made by the authors show—I. That α-thiotolen from coal-tar is a mixture of β- and γ-thiotolen. II. That there are only two thiotolenic acids which are chemically different from one another, the β-acid melting at 126·5°, and the γ-acid which melts at 136°. The α-acid melting at 118° is chemically identical with the β-acid; it yields the same bromo-derivative (Abstr., 1885, 1206), and the calcium salts of both acids yield, when distilled, the same ketone (compare p. 229). III. That α-tribromothiotolen melting at 74° is formed by the joint crystallisation of the β- and γ-compounds; when once formed, it cannot be resolved into its constituents.

These results remove the objections to V. Meyer's formula for thiophen (which admits of only two series of mono-derivatives), caused by the apparent existence of three series of derivatives.

N. H. M.

Monobromothiophen and Ethylthiophen. By E. Schleicher (*Ber.*, **18**, 3015—3023).—When monobromothiophen (Abstr., 1883, 1091) is treated with ethyl bromide and sodium, it yields β-ethylthiophen.

Ethylthiophenic acid, $C_4SH_2Et\cdot COOH$, is prepared by the action of iodine and mercuric oxide on ethylthiophen, and subsequent treatment of the iodo-ethylthiophen thus formed with ethyl chlorocarbonate and sodium amalgam. It forms colourless, lustrous crystals, readily soluble in alcohol and ether, and melts at 71°. The *calcium salt* (with $2\frac{1}{2}$ mols. H_2O) forms colourless needles with a silky lustre. The *silver salt* forms a white, curdy precipitate. When ethylthiophenic acid is oxidised by potassium permanganate, a thiophendicarboxylic acid (Abstr., 1885, 767) is obtained.

Acetoethylthiënone, C_4SH_2EtAc, is obtained by treating a mixture of 33 grams of ethylthiophen, 20 grams of acetic chloride in 160 grams light petroleum with about 30 grams of aluminium chloride; it forms an almost colourless liquid, having an agreeable odour; the *hydroxylamine-derivative* melts at 110°. *Nitracetoethylthiënone*, $NO_2\cdot C_4SHEtAc$, forms white, lustrous needles, melting at 71°, readily soluble in boiling water, alcohol, and ether. When an alcoholic solution is

treated with a trace of soda, it acquires a splendid purple colour. Acetoethylthiënone, when oxidised, yields a dicarboxylic acid identical with that obtained from ethylthiophenic acid. N. H. M.

Derivatives of Brominated Thiophens. By J. Rosenberg (*Ber.*, **18**, 3027—3031; compare Abstr., 1885, 1051). — *Tribromothiophen sulphochloride*, $C_4SBr_3 \cdot SO_2Cl$, is prepared by boiling a weighed quantity of the sulphonic anhydride and the necessary amount of phosphoric chloride with phosphorus oxychloride. It crystallises in yellowish-white, hard needles, melting at 126°. *Tribromothiophensulphonamide*, $C_4SBr_3 \cdot SO_2NH_2$, is obtained from the above compound by the action of ammonium carbonate. It forms white needles.

Tribromonitrothiophen, $C_4SBr_3 \cdot NO_2$, is obtained by the action of fuming nitric acid on tribromothiophen, suspended in sulphuric acid. It crystallises in matted, reddish-yellow needles, which melt at 106° and are readily soluble in ether, sparingly in alcohol. When fused tribromothiophen suspended in sulphuric acid is treated with fuming nitric acid, dinitrodibromothiophen is formed identical with that already obtained from dibromothiophen.

The author endeavoured to obtain an isomeric thiophendicarboxylic acid by distilling with potassium cyanide the thiophendisulphonic acid obtained by the sulphonation of dibromothiophen and subsequent removal of the bromine from the dibromo-disulphonic acid so obtained (this acid being isomeric with that obtained by the direct sulphonation of thiophen), but mere traces of a nitrile were formed. Several substances described by Langer (*Ber.*, **17**, 1566) were obtained in a state of purity, and the following corrections are made :—Dibromothiophen sulphochloride, $C_4SHBr_2 \cdot SO_2Cl$, is a crystalline solid, and melts at 32—33° ; dibromothiophen disulphochloride, $C_4SBr_2(SO_2Cl)_2$, melts at 219—220°. N. H. M.

Methylacetothiënone. By R. Demuth (*Ber.*, **18**, 3024—3026). —*Methylacetothiënone*, $C_4SH_2Me \cdot COMe$, is prepared by the action of aluminium chloride on β-thiotolen and acetic chloride dissolved in light petroleum. It forms a pale red oil boiling at 224° (corr). The *hydroxylamine-derivative* crystallises in small, colourless needles melting at 119°. Phenylhydrazine and sodium acetate act on methylacetothiënone with formation of a compound melting at 131°. When methylacetothiënone is treated with well-cooled fuming nitric acid, a *nitro-compound*, $NO_2 \cdot C_4SHMe \cdot COMe$, melting at 125°, is obtained. When methylacetothiënone is oxidised, it yields thiophendicarboxylic acid. γ-Methylthiophen behaves like the β-compound when acetylated and yields a ketone boiling at 216° (corr.).

N. H. M.

α- and β-Thiënone. By L. Gattermann (*Ber.*, **18**, 3012—3015). —*β-Thiënone*, $CO(C_4SH_3)_2$, is prepared by the action of carbonyl chloride on thiophen ; the product is diluted with an equal volume of light petroleum, cooled and treated with aluminium chloride. It is readily soluble in warm alcohol, crystallises in colourless needles, melts at 87—88°, and boils at 326° (uncorr.). The *hydrazide* crystallises in nodules and melts at 137°. β-Thiënone was also prepared by

distilling calcium β-thiophenate. The same ketone is obtained by the distillation of calcium α-thiophenate. N. H. M.

γ-Thiophenic Acid. By F. Muhlert (*Ber.*, **18**, 3003—3005).—This acid was obtained by oxidising thiotolen (Abstr., 1885, 1051). It crystallises from water in colourless needles melting at 136°. The *calcium salt* (with $\frac{1}{2}$ mol. H_2O) forms colourless needles; the *silver salt* crystallises in lustrous needles, sparingly soluble in water.

Concentrated nitric acid acts on γ-tribromothiotolen with formation of a compound, $C_4SBrMe(NO_2)_2$, melting at 125°; it crystallises in short yellow prisms. N. H. M.

Chlorobenzenes. By Istrati (*Ann. Chim. Phys.* [6], **6**, 367—395).—Chlorine acts on benzene in the presence of sunlight, forming only additive compounds in the first place. When the benzene is saturated in this manner, substitution-compounds are formed, and possibly all the hydrogen may be thus replaced and hexachlorobenzene hexachloride obtained. By acting on benzene with excess of chlorine in this manner and boiling the products obtained with alcoholic potash, in addition to 1, 2, 4 trichlorobenzene and penta- and hexa-chlorobenzenes, the author has obtained 1, 3, 4, 5 tetrachlorobenzene in the pure state in considerable quantity (about 14 per cent. of the crude chlorobenzenes treated). It melts between 28° and 30°, remains in a state of superfusion to a little below 20°, and boils at 242—243°. A. P.

Separation of Mixtures of Hydrocarbons of the Benzene Series. By C. Friedel and J. M. Crafts (*Compt. rend.*, **101**, 1218—1223).—The method described in this paper was devised for the purpose of separating ethylbenzene and the three xylenes which are formed, together with other products, by the action of aluminium chloride on toluene. It is based upon the fact that dry bromine containing 1 per cent. of iodine converts all the xylenes completely into tetrabromo-derivatives and ethylbenzene into a dibromo-derivative, the latter being subsequently converted into pentabromethylbenzene by the action of bromine in presence of aluminium chloride or bromide. Pentabromethylbenzene was obtained by Gustavson, but was not described. It crystallises in monoclinic prisms which melt at 141·5°, and can be distilled with considerable decomposition under ordinary pressure. Under a pressure of 160 mm., it distils unchanged. Pentabromethylbenzene is soluble in 11 parts of light petroleum (b. p. 80—90°) at 20°, and the dibromo-derivative is miscible with light petroleum in almost all proportions. The tetrabromo-xylenes require about 200 parts of light petroleum for solution; hence this liquid can be employed to separate the various products.

The mixture of hydrocarbons is mixed with about 10 times its weight of bromine containing 1 per cent. of iodine and allowed to remain for 10 hours at the ordinary temperature. The excess of bromine is removed by means of potash, and the dried product exhausted with successive portions of light petroleum until the dissolved matter melts at a higher temperature than 240°. The petro-

leum is concentrated repeatedly until the tetrabromo-xylenes have almost completely crystallised, and the quantity remaining in solution is calculated from the known solubility of these compounds. The petroleum is expelled from the mother-liquor by evaporation, the residue is mixed with four or five times its weight of bromine, and aluminium chloride or bromide is added. After some hours the product is washed with potash, crystallised from benzene, and weighed, a correction being made for the small quantity of admixed tetrabromo-xylenes.

About 10 per cent. of ethylbenzene was isolated by this method from the product boiling at 137°, obtained by heating toluene at 110° for two days with 20 per cent. of aluminium chloride. The analysis can be made with 5 grams of matter, or even less.

Ethylene and its homologues are formed by the condensation of the methylene which is liberated in the reaction, thus: $2C_6H_5{\cdot}CH_3 = 2C_6H_6 + C_2H_4$, and the ethylbenzene is produced by the reaction $C_6H_6 + C_2H_4 = C_6H_5{\cdot}C_2H_5$.

In order to separate the xylenes, about 2 grams of the tetrabromo-derivatives are heated in sealed tubes at 160—170° (in the vapour of pseudocumene) with 20 grams of bromine and 20 grams of water. The tetrabromo-derivatives are converted into the theoretical quantities of the corresponding tetrabromophthalic acids, $C_6Br_4(CH_3)_2 + 6Br_2 + 4H_2O = C_6Br_4(COOH)_2 + 12HBr$. Any destruction of the phthalic acids by further oxidation is indicated by the presence of carbonic anhydride in the tubes. The tetrabromophthalic acids are obtained in exactly the same proportions as the isomeric hydrocarbons in the mixture taken for analysis, and they can be separated by methods which will be described in a subsequent paper. The ortho-acid crystallises in small plates, requires 400 parts of water at 15° for complete solution, and is easily converted into the anhydride or the imide. The para-derivative crystallises in needles and gives a precipitate with silver solution. The meta-derivative gives no precipitate with silver, and is much more soluble than the other two.

C. H. B.

Chlorinated Ethylbenzenes. By Istrati (*Ann. Chim. Phys.* [6], **6**, 395—432).—The higher members of the series of monochlorethylbenzenes may be prepared by passing a further amount of ethylene into the mixture of phenyl and aluminium chlorides (Abstr., 1885, 251). They are all liquids which do not crystallise at 7°, and are soluble in the usual solvents.

Parachlorethylbenzene boils at 181—182°, and has a sp. gr. of 1·068. By boiling the mixed monochlorethylbenzenes (*loc. cit.*) with sulphuric acid, four isomeric sulphonic acids are formed which may be separated by the fractional crystallisation of their barium salts.

α. $2(C_6H_3ClEt{\cdot}SO_3)_2Ba + H_2O$ forms white needles, and is very sparingly soluble in water. β. $4(C_6H_3ClEt{\cdot}SO_3)_2Ba + 3H_2O$ forms a white, crystalline powder consisting of very small needles. γ. $(C_6H_3ClEt{\cdot}SO_3)_2Ba + H_2O$ forms colourless, rhombic plates having a brilliant lustre; and, lastly, δ. $3(C_6H_3ClEt{\cdot}SO_3)_2Ba + H_2O$ forms white granular or mamellar tufts of acicular crystals, and is readily soluble in water.

The mixed *monochlorodiethylbenzenes*, $C_6H_3ClEt_2$, have a sp. gr. of 1·036 at 0°, and boil between 215° and 255°; by oxidation with chromic acid two chlorophthalic acids are obtained; the α-acid [?Cl: $(COOH)_2$ = 1 : 3 : 5], is insoluble in water at 15°, but dissolves readily in boiling water and most of the ordinary solvents, and melts at 129—130°. When sublimed, it readily yields the anhydride, which crystallises in needles, melts at 114°, and is soluble in the usual solvents. The β-acid is insoluble in boiling water, but dissolves in dilute ammonia from which hydrochloric acid precipitates it in amorphous, white flocks; it is sparingly soluble in hot alcohol from which it crystallises better than its isomeride; it dissolves in most of the ordinary solvents, melts at 123°, sublimes readily at 100°, and distils without decomposition; it probably has the constitution $C_6H_3Cl(COOH)_2$ [?Cl : $(COOH)_2$ = 1 : 2 : 5]. Besides these acids, a third oxidation-product, *chlorethylbenzene methyl ketone*, $C_6H_3EtCl{\cdot}COMe$, was obtained; it is insoluble in hot aqueous ammonia, but dissolves readily in hot alcohol; boils between 265—270°; by fusion with potash it is converted into *ethylchlorobenzoic acid*, $C_6H_3ClEt{\cdot}COOH$. This is insoluble in cold water, melts at 115°, and commences to sublime at 100°; the *barium* salt, $(C_6H_3ClEt{\cdot}COO)_2Ba$, forms small crystals insoluble in cold water.

The *chlorotriethylbenzenes*, $C_6H_2ClEt_3$, boil between 235° and 260°, and have a sp. gr. of 1·028 at 8°; by oxidation with potassium permanganate, an acid was obtained in small quantities.

The *monochlorotetrethylbenzenes*, C_6HClEt_4, boil between 265° and 290°; the sp. gr. of the liquid at 0° is 1·022.

Monochloropentethylbenzene, C_6ClEt_5, is very difficult to obtain; it boils between 290° and 295°; the sp. gr. of the liquid at 0° is 1·065. In the preparation of this compound, a liquid boiling at 350° was separated; it has a reddish colour; its vapour-density is 8·85, and its sp. gr. at 0° = 1·179; it remains liquid at −7°, and has the composition $C_{18}H_{18}Cl_2$. A. P.

New Method of Chlorination. By A. Colson and H. Gautier (*Compt. rend.*, **101**, 1064—1066).—When 10 c.c. of a xylene are heated with 35 grams of phosphoric chloride in sealed tubes at about 190°, the products are phosphorous chloride, hydrogen chloride, and a chlorine-derivative. Paraxylene yields tolylene chloride, $C_6H_4(CH_2Cl)_2$; ortho-xylene yields the chloride corresponding with ortho-xylene glycol and metaxylene, the chloride corresponding with metaxylene glycol.

If 7 c.c. of toluene is heated in sealed tubes at 190° with 30 grams of phosphoric chloride it yields benzyl dichloride, $CHPhCl_2$.

5·5 c.c. of paraxylene heated under the same conditions with 40 grams of phosphoric chloride, yields phosphorus trichloride and a chloride, $C_6H_4(CHCl_2)_2$, which forms transparent crystals melting at 93°, and is soluble in ether, light petroleum, chloroform, benzene, and alcohol. When heated with 100 times its own weight of water, this chloride is converted into terephthalic aldehyde.

Ortho-xylene under the same conditions yields a corresponding derivative, which melts at 86°, is more soluble in ether and light

petroleum than the para-compound, and likewise dissolves in benzene, chloroform, and alcohol. When boiled with 100 times its weight of water, it is completely saponified, and although the corresponding aldehyde has not yet been isolated, alkalimetric titration of the liquid after saponification shows that the chloride has the constitution $C_6H_4(CHCl_2)_2$, and not $C_6H_4{\cdot}CCl_3{\cdot}CH_2Cl$.

These results show that phosphoric chloride furnishes a means of introducing a definite amount of chlorine into the homologues of benzene, and that the chlorine does not act on the hydrogen of the benzene nucleus until substitution has taken place in the lateral chains. C. H. B.

Fractions of Coal-tar Oil Boiling between 170—210°; 1, 2, 4, 5 Durene. By K. E. Schulze (*Ber.*, **18**, 3032—3034).—1500 c.c. of coal-tar oil boiling between 180 and 200°, previously freed from bases and phenols, was shaken successively with quantities of sulphuric acid of increasing strength (from 400 c.c. of 66 per cent. acid to 20 c.c. fuming acid containing 50 per cent. sulphuric anhydride) for 10 minutes and allowed to subside for a quarter of an hour in each case, when the acid was drawn off and saponified. A residue of paraffin remained. The last fraction but one yielded symmetrical durene. Other modifications of durene are probably present. These results are contrary to Jacobsen's hypothesis, which excludes the possibility of the presence of tetramethyl-derivatives of benzene in coal-tar oil. N. H. M.

Metacresol. By W. Staedel (*Ber.*, **18**, 3443—3445)—It is generally stated that metacresol does not solidify even at −80°; it is, however, here shown that when prepared pure from metatoluidine it can be made to crystallise when cooled in a freezing mixture to −18°, by the addition of minute crystals of phenol, which it resembles in crystalline form. Thus obtained it melts at 3—4°.

Similar experiments with commercial metacresol were not so successful, although it was obtained of a glassy consistency in a freezing mixture of ether and solid carbonic anhydride. V. H. V.

Derivatives of Phloroglucinol. By J. Herzig (*Monatsh. Chem.*, **6**, 884—888).—Tribromophloroglucinol was prepared from pure synthetically produced phloroglucinol, and also from the querciglucol of Gautier (Abstr., 1881, 272). As the loss in the preparation of this compound by Hlasiwetz's method is due to the simultaneous presence of bromine and water, the following modified process was adopted. Bromine was added gradually, and in slight excess, to a solution of phloroglucinol in glacial acetic acid, the free bromine removed by heating on the water-bath, and the tribromophloroglucinol recrystallised from water, the yield was 92—94 per cent. of the phloroglucinol employed. The melting points of the tribromo-compounds produced by this method from pure phloroglucinol and from querciglucol were found to be identical, namely 148—150°, and further the triacetyl-derivatives, $C_6Br_3Ac_3$, prepared from the tribromo-compounds by the action of acetic anhydride and sodium acetate, which crystallise from alcohol in colourless needles, also showed in each case the same

melting point, 181—183°. The difference, therefore, observed by Gautier between phloroglucinol and querciglucol is apparently due to the presence of impurities in the latter.

On submitting tribromophloroglucinol to the action of dilute alkalis, the whole of the bromine is removed as hydrogen bromide, and on acidifying no precipitate is formed; the products of this reaction have not yet been examined. A. P.

Phenylmelamines and their Derivatives: Normal, Iso, and Asymmetric Compounds. By A. W. Hofmann (*Ber.*, **18**, 3217—3234).—Triphenylmelamine (this vol., p. 41) is best prepared by the action of aniline on cyanuric chloride; the product is extracted with dilute hydrochloric acid to remove unchanged aniline, and then crystallised from alcohol. When heated with hydrochloric acid at 150°, it is decomposed into aniline and cyanuric acid.

Hexaphenylmelamine, $C_3N_3(NPh_2)_3$, is obtained by the action of diphenylamine on cyanuric chloride. It forms rhombic plates, melting above 300°, insoluble in alcohol, ether, chloroform, &c., but can be recrystallised from nitrobenzene. Hydrochloric acid at 150° converts it into diphenylamine and cyanuric acid.

Phenylcyanamide is prepared by heating 15 grams of phenylthiocarbamide, 25 grams of potash, 50 grams of lead acetate, and $\frac{1}{4}$ litre of water for 10—15 minutes at 100°; the solution is then filtered and treated with acetic acid. The amide separates as an oil, which solidifies on cooling. It crystallises from water (with $\frac{1}{2}$ mol. H_2O), and melts at 47° (comp. Abstr., 1879, 804; 1880, 44); a *platinochloride*, $(CN\cdot NHPh)_2,H_2PtCl_6$, and a *silver salt*, CN·NAgPh, were prepared; they differ in composition from those described by Feuerléin (*loc. cit.*).

Triphenylisomelamine, $(C:N\cdot Ph)_3(NH)_3$, is prepared by heating phenylcyanamide for one hour at 100°; it melts at 185° (comp. *Ber.*, **3**, 267). The *platinochloride* and *aurochloride* are described. When stirred with cold dilute hydrochloric acid, it gradually dissolves with formation of a compound of the formula, $NPh<^{CO\,---\,NPh}_{C(NH)\cdot NPh}>C:NH$, and much ammonium chloride. This substance, when boiled with hydrochloric acid, yields a compound $NPh<^{CO\cdot NPh}_{CO\cdot NPh}>C:NH$. This crystallises from alcohol in needles, which melt at 272°. A platinochloride, $(C_{21}H_{16}N_4O_2)_2,H_2PtCl_6$, was prepared. Hydrochloric acid at 150° converts triphenylisomelamine into triphenyl isocyanurate,

$$NPh<^{CO\cdot NPh}_{CO\cdot NPh}>CO,$$

melting at 275° (comp. Abstr., 1885, 774).

Asymmetrical triphenylmelamine, $NPh<^{C(NH)\cdot NPh}_{C(NH)\,---\,N}>C\cdot NHPh$, is obtained when a solution of phenylthiocarbamide in strong alcohol is boiled with freshly precipitated mercury oxide, filtered, and boiled for a long time in a reflux apparatus. From time to time, the alcohol is distilled off, and the resinous product treated with the cold alcohol. This is repeated until the resin no longer forms a clear solution in the

alcohol, when an additional hour's boiling suffices to complete the reaction. The product is purified by crystallisation from chloroform, and forms small colourless needles melting at 217°. It is insoluble in water, but dissolves readily in all acids, and is precipitated by the addition of alkali. The *platinochloride*, $C_{21}H_{16}N_6,H_2PtCl_6 + H_2O$, forms small, nodular, very sparingly soluble crystals. The *aurochloride* was also prepared. Hydrochloric acid acts on it at 100°, with formation of a compound, $NPh<^{CO\cdot NPh}_{C(NH)\cdot N}>C\cdot NHPh$.

The *aurochloride*, $C_{21}H_{17}N_5O,HAuCl_4$, crystallises in groups of plates.

When asymmetrical triphenylmelamine is heated at 150° with hydrochloric acid, *diphenylated orthoisocyanuric acid*, $NPh<^{CO\cdot NPh}_{CO\text{---}N}>C\cdot OH$, is formed. It is almost insoluble in water, sparingly soluble in ether and alcohol, and crystallises from the latter in groups of needles, melting at 261°; a *silver salt*, $C_{15}H_{10}AgN_3O_3$, was prepared. Concentrated hydrochloric acid at 280° decomposes the acid into aniline, ammonia, and carbonic anhydride. N. H. M.

Toluylenethiocarbimide. By O. Billeter and A. Steiner (*Ber.*, **18**, 3292—3295).—Toluylenedithiocarbamide was prepared by Lüssy's method (this Jour., 1875, 1036), slightly modified. It forms colourless lustrous plates, melting at 206° (uncorr.). Fuming nitric acid at 120° does not act on it. Hydrochloric acid acts on it with formation of a small quantity of a crystalline substance, probably toluylenethiocarbimide.

Metatoluylenediphenylthiocarbamide separates from a dilute solution of toluylenediamine and phenylthiocarbimide in a mixture of alcohol and ether in small crystals, melting at 163°. When boiled with strong hydrochloric acid, it decomposes into (1) toluylenediamine and phenylthiocarbimide, (2) aniline and *metatoluylenedithiocarbimide* (toluyleneisothiocyanate), $C_7H_6(CNS)_2$. The latter compound crystallises from light petroleum in colourless crystals melting at 56°. Its vapour has the characteristic odour of thiocarbimides.

The compound described by Lüssy (*loc. cit.*) as toluylenethiocarbimide is probably impure phenylthiocarbimide. Toluylenethiocarbimide can be more advantageously prepared by Rathke's method (*Annalen*, **167**, 218) from toluylenediamine. N. H. M.

Crystallography of some Organic Compounds. By E. Wickel (*Zeit. Kryst. Min.*, **11**, 78—82).—Crystals of the following compounds were measured: Metanitrobenzmesidine, $C_6H_2Me_3NH\cdot CO\cdot C_6H_4\cdot NO_2$, monosymmetric, $a:b:c = 1{\cdot}6983:1:2{\cdot}7838$, $\beta = 84°\ 18'$. Sodium metasulphobenzoate, $SO_3Na\cdot C_6H_4\cdot CO\cdot OH + 2H_2O$, asymmetric, $a:b:c = 0{\cdot}5123:1:1{\cdot}7144$, $\alpha = 95°\ 43'$, $\beta = 103°\ 33'$, $\gamma = 78°\ 24'$. Benzophenone, rhombic, $a:b:c = 0{\cdot}8511:1:0{\cdot}6644$. Mononitromesitylene, rhombic, $a:b:c = 0{\cdot}5600:1:0{\cdot}4878$. Ethylacetanilide, rhombic, $a:b:c = 0{\cdot}8401:1:1{\cdot}0064$. Ethyl anishydroxamate, $C_8H_7O_2NEt\cdot OH$ (Abstr., 1883, 462), monosymmetric, $a:b:c = 1{\cdot}3174:1:0{\cdot}8563$, $\beta = 86°\ 54'$. B. H. B.

Crystallographic Examination of some Organic Compounds. By O. Heintze (*Zeit. Kryst. Min.*, **11**, 83—88).—Crystals of the following compounds were measured: Trinitroparaxylene, $C_6HMe_2(NO_2)_3$, monosymmetric, $a:b:c = 2{\cdot}4134:1:1{\cdot}9194$, $\beta = 75°\ 40'$. Barium isophthalate, $C_6H_4(CO{\cdot}O)_2Ba + 6H_2O$, asymmetric,

$$a:b:c = 0{\cdot}79354:1:0{\cdot}61347,$$

$\alpha = 92°\ 39\frac{1}{3}'$, $\beta = 93°\ 48\frac{3}{4}'$, $\gamma = 78°\ 53\frac{1}{2}'$. Nitrodiethylmetamidobenzoic acid, monosymmetric, $a:b:c = 0{\cdot}89325:1:1{\cdot}09523$, $\beta = 74°\ 57'$. Trimethylmetachlorophenylammonium bromide, $C_6H_4Cl{\cdot}NMe_3Br$, rhombic, $a:b:c = 0{\cdot}87535:1:0{\cdot}53392$. Compound of grape-sugar with sodium chloride, $2C_6H_{12}O_6,NaCl + H_2O$, hexagonal, rhombohedral, $a:c = 1:1{\cdot}7523$. Paratolytrimethylammonium iodide, rhombic, $a:b:c = 0{\cdot}71747:1:3{\cdot}05495$. Triethylentritolytriamine, $N_3Et_3(C_6H_4Me)_3$, monosymmetric, $a:b:c = 0{\cdot}5816:1:1{\cdot}0309$, $\beta = 75°\ 23\frac{1}{2}'$. B. H. B.

Action of Acetone on Aniline. By C. Engler and P. Riehm (*Ber.*, **18**, 3296—3297; comp. Abstr., 1885, 1246).—A reply to Beyer (this vol., p. 145).

Action of Potassium Cyanide on Dinitromethylaniline. By E. Lippmann and F. Fleissner (*Monatsh. Chem.*, **6**, 807—817).—On slowly adding potassium cyanide (1 mol.) to an alcoholic solution of dinitrodimethylaniline (1 mol.) heated at 50°, dimethylaniline and a little ammonia are given off, the liquid becomes reddish-brown, and after a time blackish-brown crystals of the potassium-derivative of *dinitrodimethylamidophenol* separate out. The pure phenol, $NMe_2{\cdot}C_6H_2(NO_2){\cdot}OH$, prepared from this melts at 195°, is very sparingly soluble in alcohol, more readily in chloroform, and insoluble in benzene; it forms clear yellow triclinic crystals exhibiting the faces 101, $\bar{1}01$, 110, and $\bar{1}10$. The yield is about 20 per cent. of the nitro-base employed. By the action of nascent hydrogen or hydrogen sulphide, the phenol is converted into an unstable amido-compound.

The *ammonium-derivative* forms golden-yellow scales; it melts at 195°. The *potassium-derivative* crystallises in brilliant orange-red needles, is insoluble in alcohol, and sparingly soluble in water. The *silver-derivative* forms clear red crystals which become brown on exposure to light; it explodes violently when heated to 140°, and is fairly soluble in cold water. The *barium*, *lead*, and *copper* derivatives were prepared. On heating dinitrodimethylamidophenol with dilute potash, dimethylamine and the dinitroresorcinol described by Benedikt (Abstr., 1881, 1132) are formed. A. P.

Ortho-xylidines. By O. Jacobsen (*Ber.*, **18**, 3166—3168).—A reply to Wroblewsky (*Ber.*, **18**, 2904).

Compounds from Diazophenols and β-Naphthylamine. By O. Sachs (*Ber.*, **18**, 3125—3132; compare Abstr., 1885, 1238).—When an aqueous solution of orthodiazophenol is added to a cold alcoholic solution of β-naphthylamine, a compound, $OH{\cdot}C_6H_4N_3H{\cdot}C_{10}H_7$,

is formed. This is insoluble in water, soluble in alcohol, from which it crystallises in slender, red needles melting at 192—193°. The *acetyl-derivative*, $OH{\cdot}C_6H_4N_3Ac{\cdot}C_{10}H_7$, forms small red needles which melt at 198°. The *benzoyl-compound*, $OH{\cdot}C_6H_4{\cdot}N_3Bz{\cdot}C_{10}H_7$, is prepared by melting together 1 part of the β-naphthylamine-compound and 2 parts of benzoic anhydride. It crystallises from benzene in slender, red, lustrous needles melting at 183°.

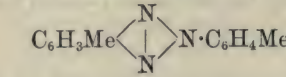
The compound $OH{\cdot}C_6H_4N_3H{\cdot}C_{10}H_7$ is decomposed by hydrochloric acid at 150—160°, with liberation of nitrogen, and formation of β-naphthylamine and pyrocatechol. Bromine acts on it, yielding dibromo-β-naphthylamine (described by Lawson, *loc. cit.*) and a brominated pyrocatechol. When reduced with zinc-dust and glacial acetic acid, it yields Lawson's α-β-naphthylenediamine.

A corresponding compound was prepared by the action of paradiazophenol on β-naphthylamine. It forms red, flat prisms melting at 192—193°, and resembles the orthophenol-derivative completely. The *acetyl-derivative* crystallises from glacial acetic acid in red, lustrous needles melting at 218°. The *benzoyl-derivative* is readily soluble in nitrobenzene, and crystallises in bright red, lustrous needles; it melts at 244°.

A *compound*, $OMe{\cdot}C_6H_4N_3H{\cdot}C_{10}H_7$, was prepared by the action of methyl orthodiazophenyl ether on β-naphthylamine. It crystallises from alcohol in dark red, monoclinic prisms, having a metallic lustre, and melts at 133°. In its behaviour, it resembles the two compounds above described. The *acetyl-derivative* forms very lustrous, red needles melting at 198—199°. The *benzoyl-derivative* crystallises in groups of dark red, lustrous needles which melt at 152—153°.

N. H. M.

Orthamidazo-compounds. By T. Zincke (*Ber.*, **18**, 3142—3144).—Orthamidazotoluene when oxidised behaves in the same way as the compounds from β-naphthylamine and diazo-salts (compare p. 244), and yields a very stable compound,



this forms colourless, lustrous, thin plates, readily soluble in hot alcohol, glacial acetic acid, and benzene; it melts at 125—126°. Hot acetic anhydride and cold concentrated sulphuric acid dissolve it unchanged; nitric acid appears to have no action on it. Assuming the compound to have the constitution given above, the constitution of orthamidazotoluene would be $C_6H_3Me{<}^{NH}_{NH}{>}N{\cdot}C_6H_4Me$. This formula does not, however, account for the formation of a diazo-compound from orthamidazotoluene and from its disulphonic acid, which requires the presence of an amido-group.

N. H. M.

Sulphonation of Phenylhydrazines. By A. Gallinek and V. v. Richter (*Ber.*, **18**, 3172—3178).—The sulphonation of the hydrazines can be effected by slowly adding the hydrazine base to

concentrated sulphuric acid, strong heating being avoided. Sulphonic acids, however, seem only to be formed when the para-position relatively to the hydrazine-group is unoccupied. The sulphonic acids can also be more readily prepared by the action of sulphuric acid on the sodium hydrazinesulphonates ($X{\cdot}N_2H_2{\cdot}SO_3Na$) obtained as intermediate products in the preparation of the hydrazines by the reduction of diazo-compounds with sodium sulphite and zinc-dust. Limpricht has recently obtained several of the hydrazinebenzenesulphonic acids by reducing the corresponding diazo-compounds (Abstr., 1885, 1216).

Parahydrazinebenzenesulphonic acid, $N_2H_3{\cdot}C_6H_4{\cdot}SO_3H$, crystallises in flat, lustrous needles, with $\frac{1}{2}$ mol. H_2O. Strecker stated it to be anhydrous. The barium, lead, sodium, zinc, and ammonium salts are described. Orthohydrazinetoluenesulphonic acid,

$$N_2H_3{\cdot}C_6H_3Me{\cdot}SO_3H\ [Me : N_2H_3 : SO_3H = 1 : 2 : ?5]$$

crystallises in tufts of thin needles. The barium, lead, sodium, and zinc salts are described. In correction to Bösler's statements (Abstr., 1882, 1062), it is mentioned that orthotolylhydrazine melts at 59°, not at 56°, and that the free base crystallises in needles, the hydrochloride in colourless four-sided plates.

Paratolylhydrazine when heated with sulphuric acid yields, not a sulphonic acid, but a peculiar basic substance which is precipitated in voluminous yellow flocks on addition of soda to the solution. It is being investigated.

In conclusion, the author states that the method of eliminating the hydrazine-group by boiling with a solution of copper sulphate, can also be applied to the determination of the nitrogen in these sulphonic acids or in acid solutions of their salts, the nitrogen being completely evolved in the free state. A. J. G.

Additive Products of Amarine Silver: Mono-substituted Derivatives of Amarine. By A. Claus and L. Scherbel (*Ber.*, **18**, 3077—3087; comp. Abstr., 1885, 1132).—*Amarine silver methiodide*, $C_{21}H_{17}AgN_2,MeI$, is prepared by the action of methyl iodide at the ordinary temperature on amarine silver, to which a large quantity of benzene has been added; in 2 or 3 days a greyish-black powder is formed which is washed with benzene and crystallised from chloroform. It is a white, pulverulent substance insoluble in ether, readily soluble in chloroform. It melts at 173° (uncorr.). *Amarine silver ethiodide*, $C_{21}H_{17}AgN_2,EtI$, is obtained in the same way as the above compound, and forms a white powder melting at 115° (uncorr.).

Amarine silver benzylchloride, $C_{21}H_{17}AgN_2,C_7H_7Cl$, is formed by the action of benzyl chloride on amarine silver at 100°. It is a white powder, which becomes violet on exposure to light; it melts at 250° (uncorr.). *Amarine silver propyl iodide* forms white microscopic crystals melting at 140° (uncorr.).

Methylamarine, $C_{21}H_{17}MeN_2$, is formed in the preparation of the above-mentioned methiodide. It is a white, crystalline substance readily soluble in ether, benzene, alcohol, and chloroform; it melts at 184° (uncorr.). *Ethylamarine*, $C_{21}H_{17}EtN_2$, formed in the preparation

of amarine silver ethiodide, crystallises in lustrous white plates melting at 163° (uncorr.); it dissolves sparingly in ether, readily in alcohol, benzene, and chloroform.

Bromobenzene acts on amarine silver with formation of lophine and benzene.

Monobenzoylamarine, $C_{21}H_{17}BzN_2$, is obtained by the action of benzoyl chloride on amarine silver suspended in benzene at 100°. It forms large, clear prisms readily soluble in benzene, alcohol, and chloroform, and melts at 180° (uncorr.). Caustic alkali converts it into amarine and benzoic acid. The *hydrochloride* is soluble in hot alcohol and in chloroform, and melts at 302°. The *platinochloride* forms a yellow, crystalline precipitate readily soluble in alcohol, insoluble in ether; it melts at 192°. The *dichromate* and *acetate* are also described. *Benzoylamarine benzoylchloride*, $C_{21}H_{17}BzN_2,BzCl$, separates from a solution of its ingredients in benzene as a white, crystalline powder readily soluble in alcohol, sparingly in chloroform and light petroleum. It melts at 312° (uncorr.). When benzoylamarine is boiled with alcohol, dibenzoylamarine is formed (comp. Abstr., 1883, 799). *Benzoylamarine benzylchloride*, $C_{21}H_{17}BzN_2,C_7H_7Cl$, forms small, bright rhombohedra insoluble in ether and benzene, sparingly soluble in chloroform. It melts at 351°. When boiled with alcoholic potash solution, it yields potassium chloride and *benzylbenzoylamarine*, $C_7H_7{\cdot}C_{21}H_{16}BzN_2$. This forms a white powder insoluble in alcohol, ether, benzene, &c.

Benzylamarine benzoylchloride, $C_7H_7{\cdot}C_{21}H_{17}N_2,BzCl$, is obtained by the action of benzoic chloride on benzylamarine mixed with benzene. It forms long, yellowish needles which melt at 340—350°. It is insoluble in ether, but dissolves readily in alcohol with decomposition, and is thus distinguished from its isomeride. The compound so formed, benzoylbenzylamarine, $C_{21}H_{16}(C_7H_7)BzN_2$, is insoluble in ether, alcohol, chloroform, and dilute acids. It melts at 318°.

Benzoylamarine methiodide, $C_{21}H_{17}BzN_2MeI$, melts at 318°; it dissolves in hot alcohol unchanged. The *ethiodide* melts at 354°. The author considers that the existence of the two compounds, benzoylamarine benzylchloride and its isomeride benzylamarine benzoylchloride, exclude Japp's formula for amarine, in which both nitrogen-atoms are represented as symmetrical amido-groups. The following formulæ are suggested for amarine silver and ethylamarine respectively:—

$$<\begin{matrix}CHPh{\cdot}NAg\\CHPh\text{——}N\end{matrix}>CPh, \text{ and } <\begin{matrix}CHPh{\cdot}NH\\CPh:NEt\end{matrix}>CPh.$$

N. H. M.

Preparation of Vanillin from the Gum of the Olive Tree. By A. Scheidel (*Dingl. polyt. J.*, **258**, 240).—The author obtains this substance by oxidising the gum of the olive tree. Olivil obtained by recrystallising the gum from alcohol, or its acetyl-derivative, $C_{14}H_{15}O_5Ac$, may also be employed. D. B.

Dehydrodivanillin. By F. Tiemann (*Ber.*, **18**, 3493—3496).—A characteristic reaction of vanillin is the production of a bluish-violet

coloration with ferric chloride; on heating, *dehydrodivanillin*, $OMe{\cdot}C_6H_2(OH)(COH){\cdot}C_6H_2(OH)(COH){\cdot}OMe$, separates from the liquid in white needles, insoluble in ordinary menstrua, but readily soluble in potash. It melts at 303—304°. It is derived from 2 mols. of vanillin by the abstraction of 2 atoms of hydrogen. Its formation is analogous to that of dithymol from thymol, and of cedriret from ethylic dimethylpyrogallol ether by means of the same reaction. Dehydrodivanillin, when heated with sodium methoxide and methyl iodide, is converted into the corresponding *dimethyl ether*,

$$C_{12}H_4(COH)_2(OMe)_4,$$

which crystallises in white needles melting at 131—138°, insoluble in water and alkalis, but more soluble than its parent compound in alcohol and ether. *Dehydrodiprotocatechuic acid*, $C_{12}H_4(OH)_4(COOH)_2$, obtained from dehydrodivanillin by fusion with potash, and subsequent purification by means of the calcium salt, is an amorphous flocculent substance, melting at above 300°; it is slightly soluble in water, and more soluble in alcohol. With ferric chloride, it gives the characteristic colour reactions of protocatechuic acid, with copper sulphate a brownish-red, with silver nitrate a brown, with lead acetate a voluminous white, and with zinc sulphate a white precipitate.

V. H. V.

Resacetophenone. By A. Michael and G. M. Palmer (*Amer. Chem. J.*, **7**, 275—277).—Nencki and Sieber (Abstr., 1881, 591 and 811) have given to resacetophenone the constitutional formula

$$C_6H_3(OH)_2{\cdot}CO{\cdot}CH_3,$$

whilst the authors had regarded it as more probably represented by $C_6H_4{<}^{O}_{O}{>}C(OH){\cdot}CH_3$, as it forms only a single monacetyl-derivative.

By the action of phenylhydrazine on resacetophenone in alcoholic solution, a crystalline substance is formed, melting at 159°, and having a composition agreeing with the formula

$$C_6H_3(OH)_2{\cdot}CMe : N_2HPh.$$

Thus it would seem that a carbonyl-group is present, although it was found impossible to obtain a diacetyl-derivative, even by using acetic anhydride and sodium acetate.

Nencki and Sieber were unable to obtain a hydroxyacetophenone by the action of zinc chloride on phenol and acetic acid; but by increasing the amount of zinc chloride this substance, $C_6H_4(OH)Ac$, can be prepared; it crystallises in needles, melts at 108°, and is insoluble in water, but dissolves in alcohol.

H. B.

Polythymoquinone. By C. Liebermann and M. Ilinski (*Ber.*, **18**, 3193—3201; comp. Abstr., 1878, 418).—When polythymoquinone is distilled, it is reconverted into thymoquinone, a small quantity of thymoquinol being also formed. Thymoquinone boils at 532° under 760 mm. pressure, not at about 200° as stated by Carstanjen (this Jour., 1871, 350). When polythymoquinone is heated with stannous chloride and

hydrochloric acid, or with zinc-dust and ammonia, or is distilled with zinc-dust, it is converted into thymoquinol.

Polythymoquinone phenylhydrazide, $(C_6H_2MePr<\overset{\text{O}}{\underset{N_2HPh}{}}>)_n$, prepared by boiling the quinone with phenylhydrazine hydrochloride and alcohol, crystallises in lustrous, orange, microscopic cubes, commences to decompose at 243°, and melts at 249°.

Polythymoquinone monoxime, $(C_6H_2MePr<\overset{\text{O}}{\underset{N(OH)}{}}>)_n$, is obtained by dissolving 10 grams of the quinone in 300 c.c. of 80 per cent. alcohol, adding 10 grams of hydroxylamine hydrochloride, and boiling for 2—3 hours. It is a crystalline powder, insoluble in water; it blackens at 240° and melts at 264° with decomposition; if heated quickly it explodes. Like other quinoximes, it shows feebly basic as well as acid properties. When reduced with stannous chloride, it yields amidothymol.

The *dioxime*, $(C_6H_2MePr<\overset{N(OH)}{\underset{N(OH)}{}}>)_n$, is prepared by heating the quinone with hydroxylamine hydrochloride, soda, and absolute alcohol at 145° for two hours. It is a sparingly soluble, heavy, white powder, melts with decomposition at about 290°, and closely resembles the monoxime. When reduced with stannous chloride and hydrochloric acid, it yields paradiamidocymene hydrochloride, $C_6H_2MePr(NH_3Cl)_2$; this forms colourless needles, and when oxidised yields thymoquinone.

Experiments are being made on the polymerisation of other quinones. A. J. G.

Ethyl Benzoylcyanacetate and Cyanacetophenone. By Haller (*Compt. rend.*, **101**, 1270—1273).—Ethyl benzoylcyanacetate is obtained by the action of cyanogen chloride on ethyl benzoylacetate. 2·4 grams of sodium is dissolved in 30 grams of absolute alcohol, 20 grams of ethyl benzoylacetate is added to the cooled mixture, and dry cyanogen chloride is passed into the liquid until the alkaline reaction disappears. The liquid is then filtered, concentrated by evaporation, and the residue heated with water and agitated with ether to remove unaltered ethyl benzoylacetate. The aqueous solution is supersaturated with sulphuric acid, and repeatedly agitated with ether. The ethereal solutions are concentrated by evaporation, and the ethyl benzoylcyanacetate purified by repeated recrystallisation. It forms hard transparent prisms which melt at 37·5°, and are soluble in alcohol, ether, potassium hydroxide, and sodium carbonate. Its alcoholic solution is distinctly acid and gives a red coloration with ferric salts. Like its analogues, ethyl benzoylcyanacetate combines with bases and forms salts. The barium salt forms white crystals, soluble in alcohol, but less soluble in water, and not decomposed by boiling; the calcium salt is very similar.

When treated with a saturated solution of hydrochloric acid in absolute alcohol, ethyl benzoylcyanacetate yields carbonic anhydride, ammonium chloride, ethyl acetate, and ethyl benzoate. If boiled with a large quantity of water, it yields cyanacetophenone, the decomposi-

tion being represented by the equation $COPh{\cdot}CH(CN){\cdot}COOEt + H_2O = CO_2 + C_2H_6O + COPh{\cdot}CH_2{\cdot}CN$. Cyanacetophenone has a distinctly acid reaction; it dissolves in sodium carbonate, and seems to form a crystallisable salt. C. H. B.

Derivatives of Durylic Acid. By J. U. Nef (*Ber.*, **18**, 3496—3499).—A continuation of the author's investigations of durene (this vol., p. 64). *Diamidodurylic* acid, $C_6Me_3(NH_2)_2{\cdot}COOH$, is obtained by the reduction of the corresponding dinitro-derivative. It crystallises in silky needles, melts at 221° with decomposition, is sparingly soluble in cold water, more soluble in hot, and in alcohol. When dissolved in hydrochloric acid, it is oxidised by ferric chloride into *duroquinonecarboxylic* acid, $C_6O_2Me_3{\cdot}COOH$, which crystallises in tufts of needles, soluble in ordinary menstrua; it decomposes at 130° with evolution of gas. It gives a yellow amorphous precipitate with lead acetate, and a compound with phenylhydrazine, insoluble in ether. It is the first example of a benzoquinonecarboxylic acid. On reduction with zinc-dust in alkaline solution, it is converted into the corresponding quinol, or *dihydroxydurylic* acid, $C_6Me_3(OH)_2{\cdot}COOH$, which crystallises in grouped needles, melting at 190° with decomposition. It is sparingly soluble in cold water, but more soluble in hot. The alkaline solutions are of a deep-violet colour; it is reconverted into the quinone acid by ferric chloride. V. H. V.

Benzallevulinic Acid. By H. Erdmann (*Ber.*, **18**, 3441—3443).—*Benzallevulinic* acid, $C_{12}H_{12}O_3$, is obtained by heating a mixture of benzaldehyde, levulinic acid, and sodium acetate; it forms minute, compact crystals, which do not, however, show a very definite melting point (120—125°). It dissolves in concentrated sulphuric acid with production of an intense red coloration; it is decomposed by concentrated potash with separation of benzaldehyde. When reduced in alkaline solution, it forms a γ-hydroxy-acid, decomposed on acidification into benzylvalerolactone, The author ascribes provisionally the formula $CHPh : C(CH_2Ac){\cdot}COOH$ to benzallevulinic acid. V. H. V.

Perkin's Reaction. Synthesis of a Sulphur-derivative of Cinnamic Acid. By J. M. Lovén (*Ber.*, **18**, 3242—3245).—A mixture of 15 grams of thiodiglycollic acid with 20 grams of benzaldehyde and 40 grams of acetic anhydride was heated with 5 to 10 grams of fused anhydrous sodium acetate for $\frac{3}{4}$ to 1 hour. The product was poured into water, when a thick brown oil separated which gradually became crystalline. This was treated with animal charcoal, and further purified by means of the sodium salt. The *new compound*, $COOH{\cdot}C(CHPh){\cdot}S{\cdot}C(CHPh){\cdot}COOH$, is insoluble in water, readily soluble in ether and in hot alcohol, and separates from the latter in small, pale-yellow crystals which do not melt without decomposition. The *sodium salt*, $C_{18}H_{12}SO_4Na_2 + 2\frac{1}{2}H_2O$, forms thin plates with a silvery lustre. A *bromine-derivative*, $C_{18}H_{12}Br_2SO_4$, was obtained by the action of bromine at 100° on a solution of the acid in chloroform. It is readily soluble in alcohol, from which it separates in short

yellow prisms, very similar in appearance to the original acid, only yellower and larger. N. H. M.

Introduction of the Carboxyl-group into Phenols. By S. v. KOSTANECKI (*Ber.*, **18**, 3202—3206).—The author points out that the method of directly introducing a carboxyl-group into polyhydric phenols by heating them with aqueous sodium or potassium hydrogen carbonates, only succeeds with those phenols containing two hydroxyl-groups in the meta-position relatively to one another.

Cresorcinolcarboxylic acid, $C_6H_2Me(OH)_2{\cdot}COOH$, is prepared by heating cresorcinol (1 part) with potassium hydrogen carbonate (4 parts) and water (5 to 10 parts) for 15 minutes; the product of the reaction is then acidified, extracted with ether, &c. It crystallises with 1 mol. H_2O in very long, thin, colourless, lustrous prisms, melts at 208° with evolution of carbonic anhydride, is readily soluble in ether, alcohol, and hot water, and gives a bluish-violet coloration with ferric chloride. The acid must have the constitution

$$[OH : COOH : OH : Me = 1 : 2 : 3 : 6 \text{ or } 1 : 4 : 3 : 6],$$

as the remaining possible constitution [COOH = 5] has been shown to belong to cresorsellinic acid.

Pyrogallol is also readily converted into an acid when heated with potassium hydrogen carbonate; this proved to be identical with the known pyrogallolcarboxylic acid. A. J. G.

Derivatives of Phthalide. By M. HOENIG (*Ber.*, **18**, 3447—3450).—When phthalide is heated with fuming nitric acid, it yields a *mononitro-derivative*, $NO_2{\cdot}C_6H_3{<}\overset{CO}{CH_2}{>}O$ [CO : CH_2 : NO_2 = 1 : 2 : 4], which crystallises in long, colourless needles, melting at 141°, nearly insoluble in cold water, more soluble in hot alcohol and ether. When heated with chromic acid, it yields unsymmetrical nitrophthalic acid. When reduced with tin and hydrochloric acid, it is converted into *amidophthalide*, $NH_2{\cdot}C_6H_3{<}\overset{CO}{CH_2}{>}O$ [CO : CO_2 : NH_2 = 1 : 2 : 4], which crystallises in short prisms, melting at 178°, insoluble in cold water, sparingly soluble in alcohol and ether; its *hydrochloride* crystallises in needles, and its *platinochloride* in minute rhombohedra. Nitrophthalide, when heated with phosphorus and hydriodic acid, yields the phosphate of *amidotoluic acid*, $COOH{\cdot}C_6H_3Me{\cdot}NH_2,H_3PO_4$, from which the free acid is obtained by decomposition with barium carbonate and subsequent addition of sulphuric acid. It crystallises in colourless needles, which melt at 153°, and are sparingly soluble in cold, moderately soluble in hot water and alcohol; its *copper* salt is a green precipitate, consisting of minute crystals. *Nitro-orthohydroxymethylbenzoic acid*,

$$OH{\cdot}CH_2{\cdot}C_6H_3(NO_2){\cdot}COOH \text{ [COOH : } CH_2{\cdot}OH : NO_2 = 1 : 2 : 4],$$

prepared by heating nitrophthalide with alkalis, crystallises in minute needles which melt at 129°; it is very soluble in ether, alcohol, and hot water; its *silver* salt forms grouped needles.

The corresponding *amido-derivative*, $OH{\cdot}CH_2{\cdot}C_6H_3(NH_2){\cdot}COOH$, is

best obtained from amidophthalide. When heated with fuming sulphuric acid, phthalide yields a *sulphonic acid*, $SO_3H{\cdot}C_6H_3{<}\begin{matrix}CO\\CH_2\end{matrix}{>}O$, which crystallises in colourless, deliquescent needles, very soluble in alcohol, insoluble in ether and chloroform. Its *barium* salt crystallises in colourless prisms, the *copper* salt in large, glistening, light-blue prisms, containing 2 mols. H_2O, and the *sodium* salt in hygroscopic needles. V. H. V.

Phthalyl-derivatives. By W. Roser (*Ber.*, **18**, 3115—3125).—Ethylenediphthalyl dissolves readily in boiling alkali solution to which alcohol has been added. When acidified, the solution yields ethylenebenzoylbenzoic acid melting at 172°. When ethylenebenzoylorthocarboxylic acid is treated with hydrochloric acid, it yields ethylenediphthalyl and an anhydride, $C_{18}H_{12}O_5$, (*α*-) already described by Gabriel. The *β-anhydride*, $C_{18}N_{12}O_5$, is formed when the acid is heated at 100° with hydrochloric acid for 10 hours. It is insoluble in water, readily soluble in hot alcohol, and crystallises in prisms melting at 200—202°. When boiled with alkali, it is converted (like the *α*-anhydride) into ethylenebenzoylorthocarboxylic acid. The following formulæ are proposed for the *α*- and *β*-anhydride:—

$$<\begin{matrix}C_6H_4\\CO{\cdot}O\end{matrix}{>}C(OH){\cdot}CH_2{\cdot}CH:C<\begin{matrix}C_6H_4\\O{\cdot}CO\end{matrix}{>} \text{ and}$$

$$<\begin{matrix}C_6H_4\\CO{\cdot}O\end{matrix}{>}C<\begin{matrix}CH_2{\cdot}CH_2\\—O—\end{matrix}{>}C<\begin{matrix}C_6H_4\\O{\cdot}CO\end{matrix}{>}.$$

When the double lactone, $C_{11}H_8O_4$, (Abstr., 1885, 267), is boiled, it yields carbonic anhydride and *phthalethylidene*, $<\begin{matrix}C_6H_4\\CO{\cdot}O\end{matrix}{>}C:CHMe$, which crystallises in small, lustrous plates, and melts at 67—69°. This compound is converted by boiling with alkali into *benzoylethylorthocarboxylic acid*, $COOH{\cdot}C_6H_4{\cdot}CO{\cdot}Et$. This acid was prepared by Gabriel, and described by him as propiophenoneorthocarboxylic acid.

γ-Phenylbutyric-orthocarboxylic acid,

$$COOH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH,$$

is obtained by the action of hydriodic acid and amorphous phosphorus on the double lactone (*loc. cit.*). It forms small lustrous plates which melt at 138—139°; it is sparingly soluble in water, readily in alcohol. The *barium* and *silver salts* are described.

β-Phthalimidylpropionic acid, $CO<\begin{matrix}C_6H_4\\NH\end{matrix}{>}C:CH{\cdot}CH_2{\cdot}COOH$, is obtained by the action of aqueous ammonia on the double lactone, and subsequent addition of hydrochloric acid to the solution. It is sparingly soluble in water, readily in hot alcohol, and crystallises in slender, slightly yellow needles melting at 225°. *Salts* are described.

Phthalimidylpropiolactone, $CO<\begin{matrix}C_6H_4\\NH\end{matrix}{>}C<\begin{matrix}CH_2{\cdot}CH_2\\O—CO\end{matrix}{>}$, isomeric with the compound last described, is prepared by evaporating a solution of the double lactone in strong alcoholic ammonia. It forms

small, bright, rhombic plates, which melt with decomposition at 205°; it dissolves readily in hot water and alcohol. Alkalis dissolve it readily with formation of salts of a *bibasic acid*, $C_{11}H_{11}NO_4$: the *barium*, *calcium*, and *silver salts* are described. The constitution of the acid is probably $COOH{\cdot}C_6H_4{\cdot}C(NH){\cdot}CH_2{\cdot}CH_2{\cdot}COOH$.

Diphthalsuccinanilide, $C_{30}H_{24}N_2O_4$, is contained in the aniline mother-liquor in the preparation of iso-ethylenediphthalyl (*loc. cit.*). It is readily soluble in nitrobenzene and aniline, sparingly in hot alcohol, from which it separates as a white crystalline powder; it melts at 267° with decomposition. When boiled with glacial acetic acid and hydrochloric acid, it yields *diphthalsuccindehydranilide*, $C_{30}H_{20}N_2O_2$. This is insoluble in water and alcohol, sparingly soluble in glacial acetic acid. It melts above 280°. Alcoholic solution of potash acts on it with formation of an acid not further examined.

N. H. M.

Carbostyril. By E. Erlenmeyer and J. Rosenhek (*Ber.*, **18**, 3295).—By the action of a solution of hypochlorous acid, obtained by treating a solution of bleaching powder with boric acid (Abstr., 1885, 1194) on quinoline, carbostyril was obtained together with other products. From a hot dilute aqueous solution (about 1 : 100) carbostyril crystallises with 1 mol. H_2O in very thin, long threads like asbestos; from a concentrated solution, it separates in anhydrous lustrous prisms.

N. H. M.

Constitution of the Compounds obtained from β-Naphthylamine and Diazo-salts: their Behaviour on Oxidation. By T. Zincke (*Ber.*, **18**, 3132—3141).—The fact that these compounds do not react with nitrous acid makes it improbable that they contain NH_2-groups. Oxidation experiments show that they contain two NH-groups. They probably belong to the class of compounds described by Griess as azimido-compounds. Thus the benzene-derivative (Abstr., 1885, 802) would have the constitution—

$$PhN\langle\begin{matrix}NH\\NH\end{matrix}\rangle C_{10}H_6 \text{ or } NHPh{\cdot}N\langle\begin{matrix}-NH-\\C_{10}H_6\end{matrix}\rangle.$$

Benzeneazimidonaphthalene, $PhN\langle\begin{matrix}N\\|\\N\end{matrix}\rangle C_{10}H_6$, is obtained by the oxidation of the hydroazimido-compound (from diazobenzene and β-naphthylamine) in acetic acid solution with chromic anhydride. It forms nodular groups of white, slender needles, readily soluble in glacial acetic acid, sparingly in alcohol and benzene. It melts at 107—108°.

Orthohydroxybenzeneazimidonaphthalene, $OH{\cdot}C_6H_4{\cdot}N_3{:}C_{10}H_6$, is prepared by the action of lead dioxide on a solution of the hydro-compound in dilute alkali. It crystallises in white needles having a silky lustre, and melts at 140°. It is insoluble in carbonates, but dissolves readily in hot glacial acetic acid, alcohol, benzene, and aqueous alkalis. Concentrated nitric acid and bromine act on it with formation of compounds melting respectively at 215—220° and 198—200°.

Concentrated sulphuric acid dissolves both compounds above described without change; reducing agents have no action on them.

Parahydroxybenzeneazimidonaphthalene is prepared in manner similar to the ortho-derivative. It crystallises from glacial acetic acid in three forms, and melts at 198—199°. It dissolves readily in acetic anhydride with formation of an acetyl-derivative melting at 164—165°. N. H. M.

Azonaphthalene and its Derivatives. By R. Nietzki and O. Goll (*Ber.*, **18**, 3252—3260).—α-Azonaphthalene (Abstr., 1885, 545) is best prepared by adding 5 parts of sulphuric acid to a solution of 1 part of amidoazonaphthalene in 100 parts of 95 per cent. alcohol; the theoretical amount of sodium nitrite dissolved in water is then added, the whole boiled for some hours and precipitated with water. The crude product is dissolved in hot aniline, and alcohol is added to the solution, when steel-blue crystals of azonaphthalene separate as it cools. It dissolves in sulphuric acid, yielding a blue solution; when this is heated at 183°, the colour changes to violet, and the solution acquires a splendid brick-red fluorescence.

Hydrazonaphthalene, $C_{10}H_7{\cdot}NH{\cdot}NH{\cdot}C_{10}H_7$, is obtained by boiling a solution of $1\frac{1}{2}$ parts of soda in 160—170 parts of alcohol, in which 1 part of azonaphthalene is suspended, and then adding zinc-dust until the solution is decolorised. The product is filtered directly into water containing ammonium sulphide, and the precipitate thus formed dried and extracted with benzene. It forms colourless plates melting at 275°, insoluble in water, readily soluble in alcohol, ether, and benzene. In the dry state it is stable.

Naphthidine, $NH_2{\cdot}C_{10}H_6{\cdot}C_{10}H_6{\cdot}NH_2$, is prepared by the action of stannous chloride on a solution of the azo-compound in glacial acetic acid. It crystallises from dilute alcohol in lustrous plates resembling benzidine, and melts at 198°. The *hydrochloride*, $C_{20}H_{16}N_2{,}2HCl$, forms colourless, lustrous plates; the *platinochloride* crystallises in yellow needles, which become greenish when dried; the *sulphate* forms lustrous plates. When a solution of a naphthidine salt is treated with ferric chloride or chromic anhydride, it acquires a splendid crimson colour. When warmed with chromic anhydride, it yields α-naphthaquinone and phthalic acid. The *diacetyl-derivative*, $C_{20}H_{14}N_2Ac_2$, melts above 300°, and is almost insoluble in the usual solvents. Nitrous acid converts naphthidine into a *diazo-compound*, which yields violet azo-dyes with β-naphtholsulphonic acids. The *platinochloride* is described. By converting naphthidine sulphate into the diazo-compound and decomposing the latter with alcohol, a hydrocarbon was obtained melting at 153·5°; it is probably identical with Lossen's α-α-dinaphthyl.

Dinaphthyline, $C_{20}H_{16}N_2$, is formed by treating hydrazonaphthalene with hydrochloric acid. It crystallises from benzene in colourless plates melting at 273°. The salts are readily soluble; when boiled with acids, even acetic acid, they give up ammonia and yield dinaphthylimide. When oxidised, phthalic acid is formed. The diazo-compound yielded a hydrocarbon identical with that obtained from naphthidine.

Dinaphthylcarbazole, $<^{C_{10}H_6}_{C_{10}H_6}>NH$, is prepared by boiling a strongly acid solution of dinaphthyline hydrochloride. It forms long colourless needles which melt at 216°. It sublimes without decomposition. It dissolves in sulphuric acid, forming a reddish-brown solution which becomes deep green on addition of a trace of nitric acid. The *picrate* forms red needles melting at 226°; it is decomposed by ammonia. When a solution of dinaphthylcarbazole in glacial acetic acid is treated with sodium nitrite, a *nitrosamine* is formed, which crystallises in small yellow plates melting above 300°. Acetic anhydride at 220° converts dinaphthylcarbazole into an acetyl-derivative. It forms colourless plates which melt above 300°; it is insoluble in benzene.

N. H. M.

Naphtholazobenzenes. By A. Denaro (*Gazzetta*, **15**, 405—409).—Four isomeric naphtholazobenzenes, $OH\cdot C_{10}H_6\cdot N_2\cdot C_6H_5$, are possible, namely, two derivable from α-, and two from β-naphthol. By fractional crystallisation from alcohol, the two latter are separated from the crude product of the action of potassium nitrite on aniline nitrate and β-naphthol; the one forms cherry-red prisms melting at 132° (comp. Margary, Abstr., 1885, 546), the other is a red crystalline powder melting at 120°. The former yields an acetyl-derivative, $C_{16}H_{11}N_2\cdot OAc$, as a brown crystalline substance melting at 95°.

On reduction with tin and hydrochloric acid, aniline hydrochloride and β-amido-β-naphthol ($NH_2 : OH = 2 : 3$) are formed, thus proving that the hydroxyl and azo-groupings are in the positions 2 : 3 respectively.

Of the isomeric α-naphtholazobenzenes, one crystallises in minute, red needles melting at 166°, the other is a violet powder melting at 175°. The former yields an acetyl-derivative melting at 140°, and on reduction and subsequent oxidation of the amido-naphthol formed it yields α-naphthaquinone; it is therefore a 1 : 4-derivative.

V. H. V.

2 : 3 Naphtholsulphonic Acid. By A. Claus and O. Volz (*Ber.*, **18**, 3154—3162).—The following salts of this acid are described:—Sodium salts, $ONa\cdot C_{10}H_6\cdot SO_3Na$ and $OH\cdot C_{10}H_6\cdot SO_3Na$, normal zinc salt with 2 mol. H_2O, normal lead salt with $2\frac{1}{2}$ mol. H_2O, basic lead salts, $C_{10}H_6SO_3,2PbO$ and $C_{10}H_6SO_3,2PbO,OH_2$. By the action of phosphoric chloride on the acid, at temperatures below 150°, several complex ethereal salts are obtained; at temperatures above 150°, a chloronaphthol and a dichloronaphthalene are mainly formed. The *chloronaphthol*, $C_{10}H_6Cl\cdot OH$ [$OH : Cl = 2 : 3$], is obtained by recrystallisation or sublimation in slender, colourless needles; it melts at 101° (uncorr.), and is moderately soluble in hot water and light petroleum, very readily in most other solvents.

2, 3, *dichloronaphthalene*, $C_{10}H_6Cl_2$, crystallises in lustrous plates, melts at 61·5° (uncorr.), boils at 286°, and seems to be identical with the δ-dichloronaphthalene of Clève (Abstr., 1878, 676). The oxidation of these substances was attended with great difficulty. With chromic acid, under the most favourable conditions, about

10 per cent. of a dichloronaphthaquinone was obtained, which was found to be the known dichloroquinone [O : Cl : Cl : O = 1 : 2 : 3 : 4].

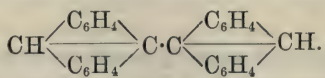
A *dinaphthylene ether*, $C_{10}H_6<^{O}_{O}>C_{10}H_6$, was obtained by heating either 2, 3, dichloronaphthalene or the corresponding chloronaphthol or naphtholsulphonic acid with sodium carbonate and potassium nitrate at 300°. It sublimes in golden-yellow, lustrous, prismatic needles, melts at 229° (uncorr.), and is soluble in chloroform, acetic acid, ether, and alcohol to sulphur-yellow solutions showing a sea-green fluorescence. A. J. G.

β-Dichloronaphthaquinone; Constitution of ε-Dichloronaphthalene. By A. Claus and P. F. Müller (*Ber.*, **18**, 3073—3076).—*β-Dichloronaphthaquinone*, $C_{10}H_4Cl_2O_2$, is obtained as an intensely yellow powder by the oxidation of ε-dichloronaphthalene (Abstr., 1882, 734). It melts at 148—149° (uncorr.), and sublimes unchanged. When boiled with alkalis, it gives up one chlorine-atom, and yields *β-hydroxychloronaphthaquinone*, $C_{10}H_4ClO_2{\cdot}OH$. This crystallises in slender, bright-yellow needles, which melt at 203° (uncorr.); it is sparingly soluble in water, readily in alcohol, ether, chloroform, and glacial acetic acid. The *alkali* derivatives form small, red crystals, readily soluble in water; the *barium* and *calcium* derivatives are bright-red, and dissolve in much water. The *silver*, *copper*, and *lead* derivatives are also described. *β-Chloronaphthaquinone-anilide*, $C_{10}H_4ClO_2{\cdot}NHPh$, is obtained by boiling an alcoholic solution of β-dichloronaphthaquinone with aniline. It forms dark reddish-violet crystals, which dissolve sparingly in alcohol, readily in glacial acetic acid. It melts at 155° (uncorr.). *β-Chloronaphthaquinone-ortho-toluide* melts at 175° (uncorr.); the *paratoluide* melts at 164° (uncorr.).

The formation of β-dichloronaphthaquinone and of a monochlorophthalic acid in the oxidation of ε-dichloronaphthalene (*loc. cit.*), show that in the latter compound the chlorine-atoms must have the β-position, and must be on different sides of the naphthalene nucleus. N. H. M.

β-Hydroxanthranole. By K. E. Schulze (*Ber.*, **18**, 3036—3039).—*β-Hydroxanthranole*, $OH{\cdot}C<^{C_6H_4}_{C_6H_4}>C{\cdot}OH$, is obtained by the action of lead peroxide on pure anthracene dissolved in glacial acetic acid. Several precautions, described in detail, have to be taken, owing to the ease with which the substance is oxidised. It resembles hydroxanthranole in most of its properties, but is distinguished by its behaviour towards an alkaline copper solution, from which it causes a separation of cuprous oxide; hydroxanthranole merely decolorises the solution. An *ethyl ether*, $C_{18}H_{18}O_2$, was prepared by boiling β-hydroxanthranole with ethyl iodide and alcohol for an hour; it forms transparent, amber-coloured crystals. The *methyl ether* crystallises in transparent, yellow, square plates, which melt at 196°. The *benzyl ether* forms lustrous, colourless crystals melting at 220°. N. H. M.

Anthrapinacone. By K. E. Schulze (*Ber.*, **18**, 3034—3036).—*Anthrapinacone*, $CH_2<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C(OH)\cdot C(OH)<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CH_2$, is prepared by acting on anthraquinone with zinc-dust and ammonia, and subsequently treating the zinc-dust with hot xylene; on cooling, this yields long, white needles of the pinacone, which resemble dihydroanthranole in appearance, but is much more sparingly soluble in alcohol. It is very electric. When heated it melts at 182°, and at the same time loses water with formation of *dianthranyl*,



N. H. M.

Chlor- and Brom-anthracenecarboxylic Acids: Action of Carbonyl Chloride on Phenanthrene. By G. Behla (*Ber.*, **18**, 3169—3171).—Graebe and Liebermann have shown (this Journ., 1872, 139) that the chloride of one of the three anthracenedicarboxylic acids is formed when anthracene is heated with carbonyl chloride at 180—200°. The author finds that at higher temperatures the known dichloranthracene, $CCl<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CCl$, and the chloride of a monocarboxylic acid are formed. This *chloranthracenecarboxylic acid*, $CCl<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C\cdot COOH$, is also obtained by the action of chlorine on a solution of anthracenecarboxylic acid in chloroform. It is crystalline, and melts at 258—259°; when heated above its melting point in sealed tubes, it is resolved into carbonic anhydride and chloranthracene. When oxidised, it yields anthraquinone.

A *bromanthracenecarboxylic acid*, crystallising in needles, has been obtained in a similar manner.

Carbonyl chloride does not act on phenanthrene at 200°; between 250° and 280° a very small quantity of a substance was obtained soluble in soda, and crystallising from benzene in needles.

A. J. G.

Crystallography of some Camphor-derivatives. By V. v. Zepharovich (*Zeit. Kryst. Min.*, **11**, 42—51).—The author gives the results of measurements of crystals of the following compounds:—Campholic acid, $C_{10}H_{18}O_2$, monosymmetric. $a : b : c = 1{\cdot}0935 : 1 : 1{\cdot}2810$, $\beta = 64° 40\frac{1}{3}'$. Nitrohydroxy-camphor, $C_{10}H_{15}(NO_2)O_2$, monosymmetric, $a : b : c = 0{\cdot}7617 : 1 : 0{\cdot}4310$, $\beta = 89° 18\frac{1}{2}'$. Bromonitrocamphor, $C_{10}H_{14}Br(NO_2)O$, rhombic, $a : b : c = 0{\cdot}7390 : 1 : 0{\cdot}4757$. Dibromonitro-camphor, $C_{10}H_{13}Br_2(NO_2)O$, rhombic, $a : b : c = 0{\cdot}8472 : 1 : 0{\cdot}5684$. Anhydrocamphoronic acid, $C_9H_{12}O_5$, rhombic, $a : b : c = 0{\cdot}9634 : 1 : 0{\cdot}8170$. Camphor-derivative, $C_8H_{12}O_4$, obtained by oxidising camphoronic acid, rhombic, $a : b : c = 0{\cdot}9877 : 1 : 1{\cdot}1236$. Silver salt of $C_8H_{12}O_4$, $C_8H_{11}AgO_4$, asymmetric, $a : b : c = 0{\cdot}5726 : 1 : 0{\cdot}5737$, axial angles, $\alpha = 92° 3' 34''$, $\beta = 95° 14' 44''$, $\gamma = 91° 52' 35''$. Potassium-derivative of dinitrobrom-

methane, $CKBr(NO_2)_2$, asymmetric, $a : b : c = 0{\cdot}7845 : 1 : 0{\cdot}6619$, $\alpha = 77° 15' 17''$, $\beta = 117° 3' 51''$, $\gamma = 98° 49' 24''$. B. H. B.

The Camphor Group. By W. Roser (*Ber.*, **18**, 3112—3115).—When camphor is oxidised with nitric acid, camphanic acid is formed as well as camphoric acid.

Ethyl camphocarboxylate, $C_{10}H_{15}O{\cdot}COOEt$, is prepared by passing hydrochloric acid into an alcoholic solution of the acid, and forms a colourless liquid boiling at 276° (uncorr.); sp. gr. = 1·052 at 15°. The boiling point excludes the possibility of the formula $C_{22}H_{32}O_6$ ascribed to the acid by Kachler and Spitzer (Abstr., 1882, 66). When sodium camphocarboxylate is treated with sodium acetate and phenylhydrazine hydrochloride, a *hydrazine compound* is formed which crystallises in needles. These results confirm the formula $C_{11}H_{16}O_3$ already ascribed to camphocarboxylic acid, and show that it is a ketonic acid. From its instability, the acid would be a β-ketonic acid. On the other hand, it may be compared with phenylglyoxylic acid, which, when distilled, yields benzaldehyde and carbonic anhydride, according to which, camphor would be an aldehyde. This would account for the formation of campholenic acid from camphoroxime, as well as from β-dibromo-camphor.

Haller's camphor cyanide may be considered as the nitrile of camphocarboxylic acid; hydroxycamphocarboxylic acid appears to have the same relation to camphocarboxylic acid that campholic acid has to camphor. N. H. M.

Camphylamine. By H. Goldschmidt (*Ber.*, **18**, 3297—3298; compare Abstr., 1885, 1072). — Camphylamine, $C_{10}H_{19}N$, was previously prepared (*loc. cit.*) by reducing the anhydride of camphoroxime with zinc and sulphuric acid. An almost theoretical yield is obtained by the action of sodium and alcohol on the anhydride. It forms a colourless liquid, which boils at 194—196° without decomposition. Exposed to the air, it solidifies to a waxy mass, consisting of a compound of camphylamine with carbonic anhydride. N. H. M.

Gutta-percha from Bassia Parkii. By E. Heckel and F. Schlagdenhauffen (*Compt. rend.*, **101**, 1069—1071).—Gutta-percha from *Bassia* (or *Butyrospermum*) *Parkii* (*Compt. rend.*, **100**, 1239) resembles ordinary gutta-percha in its physical properties. It is obtained in compact, fibrous masses, which soften in warm water and become adhesive at about the boiling point. It becomes electrified as easily as the ordinary variety, and serves equally well as an insulator; sp. gr. 0·976.

The gutta-percha from Bassia is, however, much less soluble in light petroleum, terebenthene, ether, and boiling acetic acid than the ordinary variety, but is almost equally soluble in carbon bisulphide, chloroform, benzene, and boiling alcohol of 95°.

The proportion of each variety dissolved by the different solvents is given in the following table :—

	Carbon bisulphide.	Chloroform.	Benzene.	Ether.
Ordinary gutta-percha	99·72	98·60	93·20	40·8
Gutta-percha from *B. Parkii*	97·92	98·28	92·80	20·1

	Light petroleum.	Terebenthene.	Boiling acetic acid.	Boiling alcohol of 95°.
Ordinary gutta-percha	34·0	20	19·2	7
Gutta-percha from *B. Parkii*	18·1	8	12·8	7

When analysed by Payen's method, the product from *B. Parkii* yields, gutta-percha 91·5, albane 6·0, fluavile 2·5 = 100, and is almost identical in composition with the commercial article. It leaves 1·2 per cent. of ash, which contains iron, manganese, calcium, sodium, potassium, lithium, silica, and sulphuric and carbonic acids.

Gutta-percha from *B. Parkii* is excellently adapted for the production of casts, moulds, &c. C. H. B.

Oxidation of Copaïba Balsam. By S. Levy (*Ber.*, **18**, 3206—3208). **Dimethylsuccinic Acid, an Oxidation-product of Copaïba Balsam.** By S. Levy and P. Engländer (*Ber.*, **18**, 3209—3212).—By the distillation of copaïba balsam, two fractions of nearly constant boiling point are obtained, of which the one investigated is colourless, lævorotatory, boils at 252—254°, and has a sp. gr. of 0·8978 at 24°. When oxidised with chromic mixture, it gave, in addition to acetic acid and other products not yet examined, 1½ to 2 per cent. of an acid, $C_6H_{10}O_4$, which proved to be identical with unsymmetrical dimethylsuccinic acid. A. J. G.

A Glucoside Allied to Coniferin. By F. Tiemann (*Ber.*, **18**, 3481—3493).—As it has been demonstrated that the composition of coniferin is represented by the formula

$$C_6H_3(C_3H_4{\cdot}OH)(OMe){\cdot}OC_6H_{11}O_5\ [=1:3:4],$$

and that it thus belongs to the class of phenol glucosides, experiments were made with a view to the synthesis of this glucoside indirectly from glucovanillin.

Glucoferulic aldehyde, $C_6H_3(C_2H_2{\cdot}CHO)(OMe){\cdot}OC_6H_{11}O_5\ [=1:3:4]$, obtained by heating glucovanillin with acetaldehyde in presence of soda, crystallises in needles containing 2 mols. H_2O; it melts at 200—202°, and is readily soluble in hot water, alcohol, and ether. It does not reduce Fehling's solution, and in aqueous solution is lævorotatory. It shows all the characteristic reactions of the aldehydes, giving a red coloration with rosaniline in presence of sulphuric acid, and with paradiazobenzenesulphonic acid and sodium amalgam, as also in yielding *phenylhydrazine* and *aldoxime* derivatives. The former,

$$OMe{\cdot}C_6H_3(C_2H_2{\cdot}CH:N_2HPh){\cdot}OC_6H_{11}O_5,$$

is a golden-yellow powder, melting at 212°, insoluble in ether and water, readily soluble in alcohol. The latter,

$$OMe{\cdot}C_6H_3(C_2H_2{\cdot}CH:N{\cdot}OH){\cdot}OC_6H_{11}O_5,$$

crystallises in white needles, melting at 163°, sparingly soluble in cold water, more soluble in alcohol.

Ferulic aldehyde, $OMe{\cdot}C_6H_3(C_2H_2{\cdot}CHO){\cdot}OH$, is best obtained by the decomposition of the above glucoside with emulsin. It is best, although very imperfectly, separated from the accompanying vanillin by the difference of solubility of their sodium hydrogen sulphite compounds. Its melting point, 84°, is close to that of vanillin, 81°; but its crystalline form is very different, in that it forms needles belonging probably to the monosymmetric system, $a : b : c = 3{\cdot}014 : 1 : ?$. It is sparingly soluble in cold water, readily soluble in alcohol and ether. As regards the ready transformation into vanillin, ferulic aldehyde resembles coniferyl alcohol.

Experiments on the reduction of glucoferulic aldehyde do not seem to have led to any very definite results.

Glucoferulic methyl ketone, $OMe{\cdot}C_6H_3{\cdot}(C_2H_2{\cdot}COMe){\cdot}OC_6H_{11}O_5$ [= 1 : 3 : 4], prepared from glucovanillin and acetone, crystallises in golden-yellow needles containing 2 mols. H_2O; it melts at 207°, is sparingly soluble in cold water, more soluble in hot water and alcohol. Its aqueous solution is lævorotatory. It yields a phenylhydrazine-derivative as a golden precipitate, and also a ketoxime. It is decomposed by emulsin into dextrose and *ferulic methyl ketone*,

$$OMe{\cdot}C_6H_3(C_2H_2{\cdot}COMe){\cdot}OH,$$

which forms clear golden needles, melting at 130°, soluble in alcohol, ether, and benzene. V. H. V.

Quercetin and its Derivatives. By J. Herzig (*Monatsh. Chem.*, 863—883).—The author considers that the formula $C_{24}H_{16}O_{11}$, adopted for quercetin is probably incorrect, and that, almost beyond doubt, the so-called quercetin-derivatives (tribromo-compounds, &c.) can no longer be considered as substitution-compounds, in which the quercetin nucleus exists in an unaltered state. This view is supported by the fact, that the most carefully executed analyses of tribromoquercetin and tribrom-octacetylquercetin give results always differing very much from the theoretical, and that both the so-called tribromoquercetin and also quercetin itself, when submitted to the action of excess of bromine in acetic acid, are converted into tribromophloroglucinol, instead of yielding a more highly brominated quercetin compound; warm dilute alkalis act on tribromoquercetin, removing the bromine as hydrobromic acid and forming an uncrystallisable substance, a reaction exactly similar to that which takes place with tribromophloroglucinol (compare this vol., p. 232). The last two reactions seem to indicate the presence of a phloroglucinol nucleus in quercetin.

By boiling quercetin with dilute alcoholic potash for from 8 to 10 hours, phloroglucinol and protocatechuic acid are obtained as end-products, and by oxidising quercetin with potassium chlorate and hydrochloric acid, protocatechuic acid is formed in abundance. The author further points out that a series of estimations of quercetin, in a large number of most carefully purified samples of quercitrin coming from various sources, have invariably given results from 2 to 3 per cent. higher than those of Liebermann and Hamburger

(Abstr., 1879, 945) and of Rigaud (*Annalen*, **90**, 283). The author has not discovered any satisfactory method for the determination of the isodulcitol, and considers it to be still an open question as to whether the products of the decomposition of quercitrin by sulphuric acid consist simply of quercetin and isodulcitol. The amount of isodulcitol which he finds varies between 34·7 and 38·6 per cent. Quercitrin is decomposed by the action of dilute acetic acid, but is not acted on by hydrogen sulphide. It is converted into an acetyl-derivative by the action of acetic anhydride and sodium acetate; this is an amorphous compound, which melts below 100°, and is much more readily soluble in alcohol than the acetylquercetin compound.

A. P.

Rhamnetin. By J. Herzig (*Monatsh. Chem.*, **6**, 889—890).—The author considers that rhamnetin is a compound very closely allied to quercetin, and that the formula $C_{12}H_8O_5$ given by Liebermann and Hörmann (Abstr., 1879, 271) should be doubled; further, the acetylrhamnetin prepared by these authors contains six molecules of acetyl on the double formula, and not four, as stated by them. By digesting ethyl-rhamnetin with potash in a sealed tube, the formation of diethylprotocatechuic acid and a derivative of phloroglucinol was observed.

A. P.

The Colouring Matter of Cochineal. By W. Will and H. Leymann (*Ber.*, **18**, 3180—3193).—The constitution of carminic acid is still practically undetermined, those substances of known constitution that have been prepared from it, such as nitrococcusic acid (trinitrocresotic acid $[(NO_2)_3 : Me : OH : COOH = 2 : 4 : 6 : 1 : 3 : 5]$ or coccinin, ruficoccin, and ruficarmin (shown by Liebermann to be anthracene-derivatives) having been obtained by such energetic reactions as may have led to considerable modifications in the component groups. The object of the present investigation was to obtain derivatives standing in closer relation to the original colouring matter. According to Hlasiwetz and Grabowski (*Annalen*, **141**, 329), carminic acid is a glucoside, and when heated with dilute sulphuric acid is resolved into a sugar and carmine-red, $C_{11}H_{12}O_7$. These statements, however, require confirmation.

When carmine-red is dissolved in aqueous (50 per cent.) acetic acid, and the solution boiled with excess of bromine, two bromo-compounds are formed, of which one, *α*-bromocarmin, crystallises on cooling, whilst the other, *β*-bromocarmin, separates in clear yellow flocks on adding water to the filtrate.

α-Bromocarmin, $C_{10}H_4Br_4O_3$, after purification, crystallises in colourless needles, melts at 247—248° with decomposition, is insoluble in water, sparingly soluble in hot alcohol, benzene, and glacial acetic acid. It is soluble in the alkaline hydroxides, but not in alkaline hydrogen carbonates.

α-Hydroxybromocarmin, $C_{10}H_6Br_2O_5 = OH{\cdot}C_9H_4Br_2O_2{\cdot}COOH$, is obtained by boiling the *α*-bromo-compound with strong aqueous potash, and is precipitated on acidifying with dilute hydrochloric acid. It forms colourless crystals, and melts at 207—208° with

evolution of gas. From its behaviour when methylated, it would seem to contain both a hydroxyl and a carboxyl group. The *methyl salt*, $OH{\cdot}C_9H_4Br_2O_2{\cdot}COOMe$, prepared by treating the above compound with methyl alcohol and hydrogen chloride, is crystalline, and melts at 192°. A *dimethyl salt*, $OMe{\cdot}C_9H_4Br_2O_2{\cdot}COOMe$, is prepared by heating α-hydroxybromocarmin with methyl alcohol, methyl iodide, and potash; it is crystalline, melts at 185°, and when boiled with alcoholic potash and acidified with hydrochloric acid, yields the *methoxy-acid*, $OMe{\cdot}C_9H_4Br_2O_2{\cdot}COOH$. This forms voluminous crystalline flocks, and melts at 185°, is insoluble in water, very readily soluble in acids. At the same time as the dimethyl salt, another compound is formed melting at 150°, from which, by boiling with potash, &c., a crystalline acid melting at 171° is obtained, and is still under investigation.

When α-hydroxybromocarmin is oxidised with an alkaline solution of potassium permanganate, an acid of the formula $C_9H_6Br_2O_4$ is obtained, together with another substance, $C_9H_4Br_2O_4$, which will be described with the derivatives of β-bromocarmin. The acid, $C_9H_6Br_2O_4$, forms colourless crystals and melts at 243—244°. The *methyl salt*, $OH{\cdot}C_8H_4Br_2O_4{\cdot}COOMe$, forms compact, colourless crystals and melts at 201°. The *dimethyl salt*, $OMe{\cdot}C_8H_4Br_2O{\cdot}COOMe$, forms lustrous crystals, melts at 161°, and is soluble in alcohol.

β-Bromocarmin could not be crystallised directly from any solvent, nor otherwise purified, but by boiling it for a short time with potash a red, powdery, potassium salt, $C_{11}H_3Br_3O_4K_2$, is formed, from which, by the action of hydrochloric acid, an acid crystallising in lustrous needles and melting at 232° is obtained. This acid, *β-hydroxybromocarmin*, is distinguished from those previously described by the fact that all its salts are highly coloured; it has the formula $C_{11}H_5Br_3O_4$. Attempts to prepare its methyl-derivatives were unsuccessful. When oxidised in alkaline solution with dilute potassium permanganate, it yields two substances which can be separated by treatment with water, in which one only is soluble.

Dibromhydroxymethylbenzoyldicarboxylic acid,

$$C_{10}H_6Br_2O_6 = ?\ COOH{\cdot}C_6Br_2Me(OH){\cdot}CO{\cdot}COOH,$$

the substance soluble in water, crystallises with 1 mol. H_2O in colourless, lustrous prisms, melts at 230° with decomposition, and is very readily soluble in most solvents. Several of its salts have been prepared.

Dibromohydroxymethylphthalic anhydride,

$$C_9H_4Br_2O_4 = OH{\cdot}C_6MeBr_2{<}\begin{matrix}CO\\CO\end{matrix}{>}O,$$

the second oxidation-product, is also obtained, as previously mentioned, by the oxidation of α-hydroxybromocarmin; it is a crystalline solid, melts at 195°, is readily soluble in alcohol, insoluble in water. It dissolves in alkalis, but not in sodium hydrogen carbonate except on long boiling. When digested for 5—6 hours with methyl iodide, methyl alcohol, and potash, it is converted into a *methyl salt* of the formula $OMe{\cdot}C_6MeBr_2(COOMe)_2$, which is crystalline, melts at 70°,

and is readily soluble in alcohol, ether, and benzene, insoluble in water and in cold alkalis. When saponified with alcoholic potash, &c., it gives *dibromomethoxymethylphthalic acid*, $OMe{\cdot}C_6MeBr_2(COOH)_2$; this crystallises in slender needles, and melts at 100° with loss of water and conversion into the corresponding *anhydride*,

$$OMe{\cdot}C_6MeBr_2{<}\begin{matrix}CO\\CO\end{matrix}{>}O,$$

a crystalline substance melting at 144°, and giving with sulphuric acid and phenol a similar colour reaction to that obtained with phthalic anhydride. When treated with potash, it is reconverted into the acid. As these results point clearly to the contiguous position of the carboxyl-groups, and as the relative positions of carboxyl to methyl and hydroxyl have already been determined in nitrococcusic acid, it follows that the hydroxy-anhydride must have the constitution [Me : C_2O_3 : Br : OH : Br = 1 : 2, 3 : 4 : 5 : 6].

If carmine-red really has the composition $C_{11}H_{12}O_7$, β-hydroxybromocarmin, which contains the same number of carbon-atoms, must stand in very close relation to it; and although not itself a coloured substance, yet when dissolved in alkali, mixed with stannous chloride, and acidified with hydrochloric acid, it yields a substance which when exposed to air in ethereal solution absorbs oxygen, yielding a coloured liquid of tint similar to that of a cochineal solution, which dyes a similar colour, and also, like a cochineal solution, turns violet-red on addition of an alkali. A. J. G.

Action of Chlorophyll on Carbonic Anhydride when removed from Vegetable Cells. By P. Regnard (*Compt. rend.*, **101**, 1293—1295).—Water containing carbonic anhydride was mixed with Coupier's solution exactly decolorised with sodium hyposulphite, the chlorophyll was added, and the vessel, completely filled, was placed in sunlight or in the dark. The decomposition of the carbonic anhydride was shown by the solution becoming blue. An entire leaf in sunlight quickly caused a blue coloration. Some tender leaves were triturated with enamel powder, treated with water, and the solution filtered. The filtrate contained chlorophyll and fragments of cellules, but no intact cells. A small quantity readily produced a coloration in the test-solution. Chlorophyll was extracted from other leaves by means of ether or alcohol, and cotton-wool was dipped into the filtered solutions and then thoroughly dried in a vacuum at the ordinary temperature. Fragments of this prepared wool were introduced into the test-solution and exposed to light; a blue coloration was quickly produced. It follows, therefore, that chlorophyll has the power of decomposing carbonic anhydride even when not enclosed in a vegetable cell and not in contact with the white protoplasm. The chlorophyll in fact stands in the same relation to the protoplasm as the hæmoglobin in the blood does to the colourless globulin.

C. H. B.

Lokao or Chinese Green. By R. Kayser (*Ber.*, **18**, 3417—3429).—This dye, imported from China, is obtained from the bark of various species of buckthorn; according to the researches of Cloez and

Guignet (this Journal, 1872, 706) it is in the crude state, a lake containing 26 per cent. of mineral matter, and from which a compound lokaïn, $C_{28}H_{34}O_{17}$, is extracted by ammonia. In this paper, these experiments are repeated but with slightly different results. On exhausting lokao frequently with ammonium carbonate, and adding 90 per cent. alcohol, a deep blue precipitate is obtained; this is the ammonium salt of *lokaonic acid*, $C_{42}H_{48}O_{27}$, from which the acid may be obtained by decomposition with oxalic acid. Thus produced, it is a pulverulent, bluish-black mass of metallic lustre, insoluble in water, alcohol, and ether. Its *monammonium* salt, $C_{42}H_{47}O_{27}{\cdot}NH_4$, forms small crystals of bronze-like lustre; the *diammonium* salt is of similar appearance; the *potassium*, *barium*, and *lead* salts are deep blue powders. Soluble compounds of lokaonic acid show a perfect absorption in the red and yellow portions of the spectrum.

Lokaonic acid, when boiled with dilute acids, is decomposed into *lokanic acid*, $C_{36}H_{36}O_2$, and a carbohydrate, *lokaose*, $nC_6H_{12}O_6$. The former is a violet, crystalline powder insoluble in water, alcohol, and ether; it gives off a molecule of water at 120°; its *ammonium* salt, $C_{36}H_{35}O_{21}NH_4$, is a dark blue powder, soluble in water to form a bluish-violet solution; the *barium* and *lead* salts, $C_{36}H_{34}M''O_{21}$, are insoluble, blackish-blue powders.

The soluble compounds of the acid show a characteristic absorption in the yellow and yellow-green portions of the spectrum.

The decomposition of lokaonic acid is expressed thus: $C_{42}H_{48}O_{27} = C_{36}H_{36}O_{21} + C_6H_{12}O_6$. Concentrated sulphuric acid converts lokanic acid into a substance of the composition $C_{36}H_{26}O_{16} = C_{36}H_{36}O_{21} + 5H_2O$, a red-brown powder, forming a barium-derivative, $C_{36}H_{24}BaO_{16}$, whilst potash decomposes it into phloroglucinol and *delokanic acid*, $C_{15}H_9O_6$, a brown powder; dilute nitric acid yields nitrophloroglucinol and a brown powder which was not further examined.

Lokaose, $C_6H_{12}O_6$, obtained in the filtrate from the insoluble lokaonic acid in the reaction mentioned above, forms minute, acicular crystals, and is distinguished from dextrose by its cupric oxide reducing power $R_x = 50$, and its optical inactivity. V. H. V.

New Constituents of Atropa Belladonna. By H. Kunz (*Arch. Pharm.* [3], **23**, 722—735).—The occurrence of a fluorescent compound in belladonna has been repeatedly noticed. The author has found this compound both in the extract of the root and of the leaves and stalk; the root extract was acidified until all fluorescence disappeared, and then agitated with ether. The brownish-yellow residue left on evaporation of the ethereal solution consisted of microscopic prisms having an acid reaction. By washing with cold ether, a non-crystallisable, bitter mother-liquor was separated, which was reserved for further examination. The crystals were purified by repeated treatment with boiling absolute alcohol, which finally yielded small clusters of light yellow, four-sided, highly refractive, rhombic prisms. This substance the author names provisionally *chrysatropic acid*, $C_{12}H_{10}O_5$. It melts at 201·5°, resolidifies at 182·6°. When carefully heated, the acid sublimes without decomposition, but when more strongly heated burns with a luminous flame leaving no residue. It

is soluble in 70—80 parts of hot water, sparingly in cold water and in ether, more soluble in alcohol and acetic acid. The concentrated aqueous and alcoholic solutions are pale yellow by transmitted light, but by reflected light show a beautiful emerald-green fluorescence; dilute solutions give a bluish fluorescence. The crystals dissolve in alkalis or alkaline carbonate solutions, yielding splendid bluish-green fluorescent solutions. An aqueous solution when treated with potassium permanganate gives a green liquid showing strong indigo-blue fluorescence. Ferric chloride gives an emerald-green coloration changing to cobalt-blue. The lead and copper salts were examined and described. From the formula and reactions of the substance, the author infers a near relationship to hydroxynaphthaquinone.

Leucatropic acid, $C_{17}H_{32}O_5$, is obtained from the bitter mother-liquor previously mentioned; it crystallises in clusters of microscopic prisms having a satin-like lustre, it melts at 73·8°, and resolidifies at 60·2°. It is insoluble in cold, but somewhat soluble in boiling water, it is nearly insoluble in cold, but readily soluble in boiling ether and in alcohol. Qualitative examination indicates that the compound belongs to the fatty acid series.

The author also found about 0·6 per cent. of succinic acid in belladonna extract prepared from the herbaceous part of the plant.

J. T.

α- and γ-Picolines. By O. Lange (*Ber.*, **18**, 3436—3441).—*α-Picoline* is best separated from animal oil by means of its sparingly soluble mercuriochloride; the process is more practical than that of the fractional crystallisation of the α- and β-picoline platinochlorides proposed by Weidel. The pure base boils at 129—130° (134° Weidel); its sp. gr. at 0° compared with water at 4° is 0·9656; its *platinochloride* forms small crystals which melt at 178°, its *mercuriochloride* leaflets which melt at 104°; its *aurochloride* crystallises in needles melting at 167—168°, and its *picrate* in needles melting at 165°; both these last-named salts are moderately soluble in water.

γ-Picoline is best obtained synthetically by Ladenburg's process from pyridine and methyl iodide. On distilling the product obtained from pyridine methiodide, two principal fractions are obtained boiling at 127—134°, and 142—150° respectively; the former consists of α-, the latter of γ-picoline. This base, when pure, boils at 144—145° (comp. Hofmann and Behrmann, *Ber.*, **17**, 2698); its sp. gr. at 0° compared with water at 4° is 0·971. Its salts are more or less sparingly soluble in water; the *platinochloride* is crystalline and melts at 225—226°; the *aurochloride* forms leaflets melting at 205°; the *mercuriochloride* long, white needles melting at 136—138°, and the *picrate*, silky needles melting at 156—157°. On oxidation, the base is converted into isonicotinic acid.

V. H. V.

β-Picoline: Synthesis of some Homologues of Pyridine. By A. Hesekiel (*Ber.*, **18**, 3091—3100).—β-Picoline prepared from acetamide, glycerol, and phosphoric anhydride (Abstr., 1885, 812) is lævorotatory; this cannot be due to the presence of optically active impurities, as suggested by Skraup in the case of β-picoline prepared

from coal-oil. The *mercuriochloride*, $(C_6NH_7)_2,H_2HgCl_4$, crystallises in white needles which melt at 143°. The *aurochloride* forms a voluminous precipitate sparingly soluble in water; it melts at 182—184°. The *picrate* crystallises in lustrous needles melting at 145—146°; it dissolves readily in water. The *zinc* salt and the *platinochloride* are also described.

Methylethylpyridine, $C_8H_{11}N$, is prepared by heating paraldehyde with 3 parts of acetamide and 2 parts of phosphoric acid for 16—20 hours at 160°. It forms a clear, colourless oil boiling at 175—179°. The *platinochloride* crystallises in beautiful, dark orange-coloured plates melting at 180°; it is probably identical with a platinochloride obtained by Dürkopf from aldehydecollidine (Abstr., 1885, 817). The *aurochloride* melting at 72° and the *picrate* melting at 157° are described.

Parvoline was prepared in a similar way from propaldehyde, acetamide, and phosphoric anhydride.

By the action of methyl iodide in β-pipecoline (Abstr., 1885, 812) dissolved in methyl alcohol, a compound, $C_8H_{18}NI$, is formed. It is a white, crystalline substance melting at 192·5°. A *platinochloride*, $C_{16}H_{36}N_2PtCl_6$, was obtained, which when heated at 234° becomes black. N. H. M.

Constitution of Aldehyde-collidine. By E. Dürkopf (*Ber.*, **18**, 3432—3435).—In this paper it is shown that aldehyde-collidine (comp. Abstr., 1885, 817) is an ethylmethylpyridine, as evidenced by its yielding on moderate oxidation a methylpyridinecarboxylic acid, identical with the acid obtained by Hoogewerff and v. Dorp from methylquinolinic acid, and with the homoisonicotinic acid of de Coninck, as shown by its physical properties, and its conversion on further oxidation into cinchomeronic acid. The constitution of this collidine is thus represented by the formula C_5NH_3MeEt [Et : Me = 3 : 4], and its hexahydride or copellidine by the formula $C_5NH_9Me_2Et$; it must then be identical with the collidine obtained from brucine by de Coninck. V. H. V.

Identity of Böttinger's Pyridinedicarboxylic Acid with Lutidinic Acid. By E. Voges (*Ber.*, **18**, 3162—3165).—Whilst according to the received theory there can be but two pyridinecarboxylic acids which yield γ-pyridinemonocarboxylic acid (isonicotinic acid), three such acids have been described. The author has reinvestigated Böttinger's pyridinedicarboxylic acid, and finds that it is identical with lutidinic acid. There are, therefore, but two pyridinedicarboxylic acids containing one COOH-group in the γ [=3] position, namely, cinchomeronic acid [2 : 3] and lutidinic acid [1 : 3]. A. J. G.

Condensation of Cinnamaldehyde with Ammonia and Ethyl Acetoacetate. By W. Epstein (*Annalen*, **231**, 1—36).—*Ethylic benzylidenedihydrocollidinedicarboxylate*, $C_{21}H_{25}O_4N$, is formed by the action of ethyl acetoacetate and alcoholic ammonia on cinnamaldehyde. It is a white, crystalline substance, soluble in ether and in

warm alcohol. It begins to soften at 146°, and melts at 148—149°. When nitrous acid is passed into an alcoholic solution of this compound, it is oxidised and converted into *ethyl benzylidenecollidinedicarboxylate*, $C_{21}H_{23}O_4N$; this melts at 39°, and is soluble in alcohol and ether. It also dissolves easily in acids, forming crystalline salts which are decomposed by water. The *platinochloride*, $(C_{21}H_{23}O_4N)_2,H_2PtCl_6$, melts at 195°. *Benzylidenecollidinedicarboxylic acid*,

$$CHPh : CH\cdot C_5NMe_2(COOH)_2,$$

melts at 218—219° with partial decomposition. The anhydrous acid melts at 241°. It is soluble in alcohol and sparingly soluble in water, ether, and chloroform. With hydrochloric acid it forms an unstable compound which is decomposed by water. The *platinochloride*, $(C_{17}H_{15}O_4N)_2,H_2PtCl_6$, crystallises in needles. The acid forms amorphous metallic salts. When oxidised with potassium permanganate, the acid splits up into benzoic acid and a *lutidinetricarboxylic acid* which is not identical with the acid obtained by Hantzsch (Abstr., 1883, 85) by the oxidation of collidinedicarboxylic acid. The lutidinetricarboxylic acid crystallises with 1 mol. H_2O in prisms. It is sparingly soluble in the ordinary solvents—560 parts by weight of water at 8° dissolve 1 part of the acid. It decomposes at 220° without melting. Hot hydrochloric acid slowly dissolves the acid; on cooling, mono- or tri-clinic crystals of the hydrochloride are deposited. This salt is decomposed by water or alcohol. The neutral salts of the acid are sparingly soluble and generally crystallise readily. Ferric chloride produces a red coloration in a solution of the ammonium salt. The mercurous salt dissolves in hot water and is deposited from the solution on cooling in microscopic prisms.

Benzene and *lutidine*, $C_5NMe_2H_3$, are formed when the mixture of benzoic and lutidinetricarboxylic acids, obtained by the oxidation of benzylidenecollidinedicarboxylic acid, is heated with quicklime in a current of hydrogen. The properties of the lutidine obtained in this way have already been described by the author (Abstr., 1885, 815). It is an isomeride of the lutidine which Hantzsch obtained from lutidinetricarboxylic acid (Abstr., 1883, 85) and from pseudolutidostyril (Abstr., 1885, 397). On oxidation, it yields a pyridenedicarboxylic acid which closely resembles Ramsay's α-pyridinedicarboxylic acid (Abstr., 1879, 266), and the isocinchomeronic acid of Weidel and Hertzig (*Monatsh. Chem.*, 1880, 5). On distillation in a current of hydrogen, picolinic but no nicotinic acid, is formed. Picolinic acid is also formed by the action of glacial acetic acid on the acid at 160°. Hence it appears that the condensation-products of aldehydes with ethyl acetoacetate have the symmetrical constitution

$$XC\lessgtr\begin{matrix}C(COOH)\cdot CMe\\ C(COOH) : CMe\end{matrix}\gtrless N.$$

W. C. W.

Action of the Homologues of Acetaldehyde on Ammonia and Ethyl Acetoacetate. By F. Engelmann (*Annalen*, **231**, 37—71).—*Ethyl hydroparvolinedicarboxylate*, $C_5NH_2Me_2Et(COOEt)_2$, is formed on warming a mixture of ethyl acetoacetate, propaldehyde,

and alcoholic ammonia. It melts at 110°, and closely resembles ethyl hydrocollidinedicarboxylate in its properties. On oxidation with nitrous acid, it loses 2 atoms of hydrogen and is converted into *ethyl parvolinedicarboxylate*, $C_{11}H_{11}O_4NEt_2$. This compound is a colourless oil, insoluble in water. It unites with mineral acids, forming hygroscopic salts. The *platinochloride*, $(C_{15}H_{21}O_4N)_2,H_2PtCl_6$, forms red prisms soluble in water, less soluble in alcohol. It melts at 139° and begins to decompose at 185°.

Parvolinedicarboxylic acid, $C_5NMe_2Et(COOH)_2$, is obtained from the ethylic salt by saponification with alcoholic potash in closed vessels. Most of the metallic salts of this acid are easily soluble in water. The silver salt is an exception. The free acid is best prepared by the action of sulphuretted hydrogen on the silver salt. It is freely soluble in water and in alcohol, and melts at 289—290° with decomposition. The *barium salt*, $C_{11}H_{11}NO_4Ba + 3H_2O$, crystallises in plates. The *hydrochloride*, $(C_{11}H_{13}O_4N)_2,HCl + H_2O$, forms glistening prisms.

Parvoline, $C_5NH_2EtMe_2$, obtained by heating a mixture of potassium parvolinedicarboxylate and quicklime, is a colourless, highly refractive liquid. Its sp. gr. at 14° is 0·916. It boils at 186°, and is soluble in 73 parts of water at 0°, but is less soluble in warm water. The aqueous solution yields precipitates with chromic and picric acids, melting at 120°, and with solutions of zinc, lead, mercuric, mercurous, and silver salts. The *platinochloride*, $(C_9H_{13}N)_2,H_2PtCl_6$, is soluble in hot water and alcohol. It melts at 210°. The *dichromate*, $(C_9H_{13}N)_2,H_2Cr_2O_7$, begins to blacken at 180°, and melts with decomposition at 200°. It is not identical with the *α*-parvoline of Williams (*Jahrb. Chem.*, 1854, 495) and of Thenius (*ibid.*, 1861, 502), nor with the *β*-parvoline of de Coninck (Abstr., 1881, 56), nor with the base which Waage obtained from propaldehyde-ammonia (Abstr., 1884, 172).

Ethyl hydroisopropyl-lutidinedicarboxylate, $C_5NH_2Me_2Pr(COOEt)_2$, prepared by the action of alcoholic ammonia and ethyl acetoacetate on isobutaldehyde, crystallises in long prisms melting at 97°. It is soluble in absolute alcohol, ether, benzene, and chloroform, insoluble in water, and sparingly soluble in alcohol. When oxidised with nitrous acid, it yields *ethyl lutidinedicarboxylate*, $C_5NHMe_2(COOEt)_2$. This substance melts at 73° and boils at 301—302° without decomposition. On recrystallisation from warm alcohol, it is obtained in long prismatic needles which are insoluble in water. *Lutidinedicarboxylic acid* is obtained as a crystalline precipitate containing ½ mol. H_2O, on the addition of hydrochloric acid to a solution of the potassium salt. It is soluble in hot water, and sparingly soluble in alcohol and ether. The *barium* salt, $C_9H_7O_4NBa + 2H_2O$, is freely soluble in water; the *lead* salt, $C_9H_7O_4NPb + 2H_2O$, crystallises in thick prisms. The *hydrochloride*, $C_9H_9O_4N,HCl + 2H_2O$, forms prisms. A solution of potassium lutidinedicarboxylate yields precipitates with silver, mercury, copper, cadmium, zinc, and iron salts. The acid is decomposed on distillation with lime, yielding a lutidine which is identical with that obtained by Epstein (this vol., p. 257).

Ethyl hydroisobutyllutidinedicarboxylate, $C_4H_9{\cdot}C_5NMe_2H_2(COOEt)_2$, is obtained by the action of alcoholic ammonia on valeraldehyde and

ethyl acetoacetate. It is deposited from alcohol or light petroleum in long prisms, insoluble in water, but freely soluble in alcohol, ether, benzene, chloroform, and glacial acetic acid. It melts at 100°. When nitrous acid is passed into the alcoholic solution of this substance, it loses 2 atoms of hydrogen, forming *ethyl isobutyl-lutidinedicarboxylate*, $C_4H_9{\cdot}C_5NMe_2(COOEt)_2$. This compound exists as a colourless, thick liquid, insoluble in water. It boils without decomposition between 312° and 318°. The *hydrochloride*, $C_{17}H_{25}O_4N,HCl$, forms long needles: the *platinochloride*, $(C_{17}H_{25}O_4N)_2,H_2PtCl_6$, is freely soluble in water. It melts at 207—208° with decomposition.

By the action of alcoholic potash on diethyl isobutyllutidinedicarboxylate, only one ethyl-group is replaced by potash. On decomposing this potassium salt, the monethyl salt, $C_4H_9{\cdot}C_5NMe_2(COOEt){\cdot}COOH$, is obtained in prismatic crystals soluble in alcohol and water. It melts at 135°, and begins to decompose at 230°. The *mercurous* salt is obtained as a white precipitate on the addition of mercurous nitrate to a solution of the potassium salt. On warming the mixture, the precipitate dissolves, and is deposited on cooling in long needles. It is decomposed by water, and metallic mercury is precipitated. The *barium*, $(C_{15}H_{20}O_4N)_2Ba + 5H_2O$, and *calcium*, $(C_{15}H_{20}O_4N)_2Ca + 4H_2O$, salts crystallise in plates, and are freely soluble in water. The *hydrochloride*, $C_{15}H_{21}NO_4,HCl + 2H_2O$, forms monoclinic prisms, soluble in water and in alcohol. The potassium salt is converted into *isobutyl-lutidinedicarboxylic acid* by boiling with an aqueous solution of potassium hydroxide. The free acid, $C_4H_9{\cdot}C_5NMe_2(COOH)_2 + 2H_2O$, prepared from the mercurous salt, crystallises in monoclinic prisms. It dissolves in hot water and in warm alcohol. The anhydrous acid melts with decomposition at 273°. A solution of the potassium salt gives precipitates with silver, lead, zinc, cadmium, and copper salts, and also with concentrated solutions of mercurous and mercuric salts. The *barium* salt, $C_{13}H_{15}O_4NBa + 5H_2O$, is freely soluble in water. The *calcium* salt crystallises in four-sided pyramids containing 3 mols. H_2O. The *hydrochloride*, $C_{11}H_{15}(COOH)_2N,HCl$, is soluble in alcohol and in hydrochloric acid.

Isobutyllutidine, $C_4H_9{\cdot}C_5NH_2Me_2$, is a colourless liquid boiling at 210—213°, and possessing a bitter taste. Its sp. gr. at 18° is 0·8961 compared with water at the same temperature. It is more soluble in cold than in warm water. The base unites with acids, forming very deliquescent salts. The *picrate* forms yellow needles which melt at 114—115°. The *platinochloride* is crystalline. It melts at 208—209°. The *dichromate* is soluble in hot water. It is decomposed by heat without melting.

Condensation products could not be obtained by the action of acraldehyde instead of aldehyde on ammonia and ethyl acetoacetate.

Pyridine-derivatives are not obtained when ethyl acetobenzoate is substituted for ethyl acetoacetate in the preceding experiments.

No condensation product is formed by the action of sulphuric acid on ethyl acetobenzoate. W. C. W.

Dimethylquinolines. By L. Berend (*Ber.*, **18**, 3165).—The dimethylquinoline from paraxylidine sulphate, described by L. Meyer

(this vol., p. 161), has already been described by the author. The base boils at 264·5—265·5°; sp. gr. 1·0752 at 4°. The platinochloride, $(C_{11}H_{11}N)_2,H_2PtCl_6$, crystallises in reddish-yellow needles.

1 : 4 *Tetrahydrodimethylquinoline*, $C_{11}H_{15}N$, obtained by reduction with tin and hydrochloric acid, boils at 271°, and has an agreeable odour; the hydrochloride, $C_{11}H_{15}N,HCl$, crystallises in slender needles or transparent, six-sided tables. A. J. G.

Quinoline-derivatives from Propaldehyde. By K. Harz (*Ber.*, **18**, 3384—3401).—*Ethylmethyltoluquinoline* (ethyldimethylquinoline), $C_9NH_4Me_2Et$ [Me : Et : Me = 3 : 2′ : 3′], prepared from paratoluidine, propaldehyde, and hydrochloric acid, forms rhombic crystals, melting at 54°, and boiling at 287—288° under a pressure of 720 mm.; it is insoluble in water, soluble in ether, alcohol, and benzene. Many of its salts are exceedingly soluble in water; the *hydriodide* crystallises in colourless needles; the *chromate* in red needles; the *picrate* in small, yellow needles, melting at 177°; the *platinochloride* in orange-red needles containing 2 mols. H_2O; the *methiodide* with H_2O in monoclinic needles, melting at 75—76°; the *ethiodide* with $\frac{1}{2}H_2O$ in agglomerated crystals, melting at 112—114°; and the *ethoplatinochloride* with $1H_2O$ in minute, glistening crystals. The base forms a *tetrahydro-additive product*, $C_{13}H_{19}N$, a colourless, strongly refractive oil, boiling at 285—286°; its *hydrochloride* crystallises in needles; the *platinochloride* in brown leaflets, containing $2H_2O$; its *nitroso-derivative*, $C_{13}H_{18}N{\cdot}NO$, forms a crystalline mass, and gives Liebermann's reaction; its *methyl-derivative*, $C_{13}H_{18}NMe$, is an oil boiling at 275—280°, and forming a platinochloride crystallising with $2H_2O$ in needles.

With bromine, the base forms an unstable dibromo-additive product decomposed on heating with formation of a *dibromo*-substitution product, $C_{13}H_{13}Br_2N$, crystallising in white needles, which melt at 143—144°, and are insoluble in water, but soluble in ether and hot alcohol. Concentrated sulphuric acid yields a *monosulphonic acid*, $C_{13}H_{14}N{\cdot}SO_3H$, crystallising in the rhombic system, sparingly soluble in cold, more so in hot water; its *barium* salt crystallises with 1 mol. H_2O in interlaced needles, and its *lead* salt, $(C_{13}H_{14}SO_3N)_2Pb,2C_{13}H_{14}N{\cdot}SO_3H + 6H_2O$, in golden needles, very soluble in water. On fusing it with alkali, the sulphonic acid is converted into the corresponding *hydroxyl-derivative*, $C_{13}H_{14}N{\cdot}OH$, which forms colourless needles, melting at 45°, and boiling at 312—316°.

With concentrated sulphuric and nitric acids, the base yields a *mononitro-derivative*, $C_{13}H_{14}N{\cdot}NO_2$, which crystallises in the triclinic system; it melts at 109°, and is insoluble in water, but readily soluble in chloroform. Its *hydrochloride* forms dendritic, golden crystals, and its *platinochloride*, thick, reddish-golden crystals, containing 2 mols. H_2O. On reduction with stannous chloride, there is formed an *amido-derivative*, $C_{13}H_{14}N{\cdot}NH_2$, crystallising in prisms or flat needles belonging to the triclinic system; it melts at 148—149°, and is very soluble in alcohol, sparingly soluble in ether and petroleum.

Ethyltoluquinolinecarboxylic acid,

$$C_9NH_4MeEt{\cdot}COOH\ [Me : Et : COOH = 3 : 2' : 3'],$$

obtained by the oxidation of the above base with chromic acid, crystallises with 1 mol. H_2O in the triclinic system; it melts at 142—143°, and is soluble in hot water and alcohol; its solutions show a slight acid reaction. Its *sodium* salt with $3H_2O$, and *barium* salt with $\frac{1}{2}H_2O$, form interlaced needles; its *copper* salt is a crystalline, and *silver* salt an amorphous precipitate. The *ethyl* salt crystallises in needles; it is soluble in alcohol and also in water, but is saponified by it. On heating at 150°, it gives off carbonic anhydride with formation of *ethyltoluquinoline*, C_9NH_5MeEt [Me : Et = 3 : 2′], crystallising in snow-white needles, which melt at 59—60°, and boil at 270° under a pressure of 718 mm.; its salts with mineral acids are very soluble in water; its *platinochloride* crystallises in needles; its *picrate* forms minute, golden crystals, melting at 244—245°. The base is apparently isomeric with the α-ethylmethylquinoline of Kugler.

Ethylmethyltoluquinoline, $C_9NH_4Me_2Et$ [Me : Et : Me = 2 or 4 : 2′ : 3′], from metatoluidine and propaldehyde, crystallises in hexagonal leaflets belonging to the rhombic system. It melts at 40—41°, and boils at 288—292°. Its *hydrochloride* crystallises in colourless prisms; the *hydroiodide* in needles; the *picrate* in golden needles, melting at 219—220°; the *platinochloride* in minute needles containing $2H_2O$; the *methiodide* with $1H_2O$ in golden needles, and the methoplatinochloride in glistening orange-red needles.

Ethylmethyltoluquinoline, $C_9NH_4Me_2Et$ [Me : Et : Me = 1 : 2′ : 3′], from orthotoluidine and propaldehyde, forms monoclinic crystals, which melt at 44°, and boil at 279—280° under a pressure of 717 mm. Its *hydrochloride*, *hydroiodide*, *picrate*, and *methiodide* crystallise in needles, the *platinochloride* in large leaflets, and the *methoplatinochloride* in glistening orange-red needles. With tin and hydrochloric acid, it forms a tetrahydro-additive product, $C_{13}H_{19}N$, a pale yellow oil, boiling at 274—276°, and dissolving in nitric acid with production of an intense coloration; its *hydrochloride* forms colourless crystals, sparingly soluble in water. V. H. V.

Quinoline-derivatives from Normal Butaldehyde. By M. Kahn (*Ber.*, **18**, 3361—3372).—On the addition of normal butaldehyde (100 grams) to aniline (60 grams) and fuming hydrochloric acid (120 grams) distillation of the product and extraction by ether, two principal fractions are obtained, boiling at 230—250° and 280—300° respectively; the former consists of butylphenylamine, the latter of *propylethylquinoline*, $C_9NH_5EtPr^a$ [Pr^a : Et = 2′ : 3′]. The pure base is a colourless liquid, boiling at 291° under 720 mm. pressure, resembling quinaldine in odour, rapidly darkening on exposure to air, insoluble in water, but volatile in a current of steam. It is soluble in alcohol, ether, and dilute acids. Its *hydrochloride* crystallises with 2 mols. H_2O in triclinic tables, the *nitrate* with 1 mol. H_2O in long crystals; both these salts are best obtained by the gradual addition of ether to their alcoholic solutions; the *sulphate* crystallises in tufts of needles, the *picrate* in golden needles or leaflets, melting at 163°, insoluble in cold water, sparingly soluble in alcohol; the *chromate*, $(C_{11}H_{17}N)_2H_2Cr_2O_7$, in orange-yellow needles; the *platinochloride* in

yellow needles, insoluble in cold, soluble in hot water; the *methiodide* in golden needles, containing 1 mol. H_2O; and methoplatinochloride $(C_{14}H_{17}N)_2,Me_2PtCl_6$, in orange-yellow dendritic needles.

Ethylquinolinecarboxylic acid, $C_9NH_5Et{\cdot}COOH$ [COOH : Et = 2′ : 3′], is obtained by the oxidation of the above base with chromic acid. It crystallises in interlaced needles, which melt at 148° with evolution of carbonic anhydride; it is soluble in water, crystallising therefrom with ½ mol. H_2O, sparingly soluble in ether. Its *platinochloride* forms groups of needles, and its *picrate* golden needles melting at 153°, sparingly soluble in water and alcohol. The copper salt is a bluish-green precipitate, consisting of minute needles; the *silver* salt, a white amorphous precipitate.

Ethylquinoline, C_9NH_6Et [Et = 3′], obtained by the dry distillation of the above acid, is a colourless highly refractive liquid, boiling at 265° under 718 mm. pressure. Its *platinochloride* crystallises in golden needles, and its *picrate* also in needles which melt at 163° (comp. Baeyer and Jackson, Abstr., 1880, 406, and Riedel, Abstr., 1883, 1152).

Normal butylphenylamine, $NHPh{\cdot}C_4H_9$, obtained in the reaction mentioned above, is best purified by means of its nitroso-derivative; it is a colourless oil, boiling at 235° under a pressure of 720 mm., and is volatile in a current of steam. Its *hydrochloride* and *sulphate* crystallise in needles, and are very soluble in water. The *nitroso-derivative*, $NO{\cdot}NPh{\cdot}C_4H_9$, is a golden-yellow liquid, insoluble in water and dilute acids, soluble in alcohol and ether; it gives Liebermann's reaction in a most marked way; the *acetyl-derivative*, $NAcPh{\cdot}C_4H_9$, is a colourless liquid, boiling at 273—275° under a pressure of 718 mm. V. H. V.

Quinoline-derivatives from Isovaleraldehyde. By J. Spady (*Ber.*, **18**, 3373—3384).—Isovaleraldehyde and aniline, in presence of hydrochloric acid, form isobutylisopropylquinoline and isoamylphenylamine (comp. preceding Abstr.), which are best separated by means of their picrates, that of the former being insoluble, whilst that of the latter is soluble in cold alcohol.

Isobutylisopropylquinoline, $C_9NH_5Pr^{\beta}{\cdot}C_4H_9{}^{\beta}$ [$C_4H_9 : Pr^{\beta}$ = 2′ : 3′], is a liquid boiling at 295—296° under 709 mm. pressure, insoluble in water, soluble in alcohol, ether, and benzene. On the addition of nitric acid to the base, its *nitrate*, $C_{16}H_{21}N,HNO_3 + H_2O$, separates at first as an oil, but ultimately solidifies in acicular crystals; the *acid sulphate* forms pyramidal crystals belonging to the triclinic system; the *hydrochloride* with $1H_2O$, prismatic leaflets, belonging to the triclinic system; the *chromate*, long, orange-yellow needles, insoluble in cold water and dilute sulphuric acid; the *methiodide*, golden needles, containing 1 mol. H_2O, soluble in alcohol and hot water; the methoplatinochloride $(C_{16}H_{21}N)_2,Me_2PtCl_6$, reddish-golden triclinic prisms, sparingly soluble in water and dilute hydrochloric acid.

Isopropylquinolinecarboxylic acid,

$$C_9NH_5Pr^{\beta}{\cdot}COOH\ [COOH : Pr^{\beta} = 2' : 3'],$$

obtained by the oxidation of the above base with chromic acid, crys-

tallises in prismatic leaflets melting at 188—189° with slight decomposition; its *platinochloride* crystallises in orange-yellow prisms; with silver nitrate it gives a flocculent precipitate of the composition, $C_{13}H_{12},NO_3Ag + C_{13}H_{13}NO_2,HNO_3$, sparingly soluble in dilute nitric acid, and decomposed by water into its components. On distillation with lime, the acid is decomposed into quinoline and a diquinoline probably identical with that obtained by Japp and Graham (Trans., 1881, 174) and by Weidel (Abstr., 1881, 613); but when heated above its melting point, it is decomposed into carbonic anhydride and *isopropylquinoline*, $C_9NH_6Pr^\beta$ [$Pr^\beta = 3'$], a pale golden liquid, boiling at 275—280° under a pressure of 715 mm., and solidifying in a freezing mixture to a crystalline mass; it is insoluble in water, soluble in alcohol, ether, and benzene. Its *hydrochloride* and *platinochloride* crystallise in needles, the *picrate* and *chromate* in delicate golden needles.

Isoamylphenylamine, $NHPh\cdot CH_2\cdot CH_2\cdot CHMe_2$, formed in the above-mentioned reaction, is a colourless oil of pleasant aromatic odour; it boils at 242—244°, is insoluble in water, soluble in alcohol and ether. Its *hydrochloride* crystallises in prisms, its *nitroso-derivative* is an oil, soluble in alcohol and ether, and giving Liebermann's reaction; and its *acetyl-derivative*, a liquid boiling at 278° under a pressure of 720 mm., insoluble in water, soluble in alcohol and ether. The base apparently is isomeric with the amylphenylamine obtained by Hofmann from amyl bromide and aniline (*Annalen*, **74**, 153).

V. H. V.

Quinoline-aldehyde. By A. Einhorn (*Ber.*, **18**, 3465—3468).—In this paper *trichlorethylidenequinaldine*, $C_9H_6N\cdot CH:CH\cdot CCl_3$, and *quinoline-aldehyde* are described which are identical with those obtained by v. Miller and Spady (p. 265), and were prepared by the same methods. The author, however, ascribes the formula $C_{12}H_{11}NO_3$, and not $C_{12}H_9NO_2$, to the acid from the trichloro-derivative. The *platinochloride* of the aldehyde forms golden, transparent crystals, containing 2 mols. H_2O; whilst the aldehyde itself is said to melt at 103—104°, but no analyses are given of this substance.

V. H. V.

An Aldehyde of the Quinoline Series. By A. Einhorn (*Ber.*, **18**, 3144—3146).—*Trimethylquinolinealdehyde*, $C_{13}H_{13}NO + 3H_2O$, is obtained by the action of chromyl chloride on crude quinaldine, being probably formed from tetramethylquinoline present in the crude substance. It crystallises from water in splendid needles melting at 73—74°; it easily parts with its water of crystallisation, and has then the melting point 101·5°. It reacts readily with hydroxylamine and with phenylhydrazine, with formation of compounds melting at 203° and 207° respectively. It reduces ammoniacal silver solution, and is oxidised at the same time to an acid which melts at 224°.

N. H. M.

Quinoline-α-acrylic Acid. By W. v. Miller and J. Spady (*Ber.*, **18**, 3402—3405).—By the direct reaction of equal molecules of chloral and quinaldine, a trichloro-compound, $C_{12}H_8NCl_3,H_2O$, is formed, which crystallises in delicate needles melting at 144—145°; when heated with an aqueous solution of potassium carbonate, it yields

quinoline-acrylic acid, $C_9NH_6{\cdot}CH{:}CH{\cdot}COOH$ [$C_2H_2{\cdot}COOH = 2'$], which crystallises in leaflets melting at 190—195°; its *hydrochloride* crystallises in colourless needles, the *platinochloride* in prisms, and the barium salt in tufts of needles.

Quinoline-aldehyde, $C_9NH_6{\cdot}COH$ [COH = 2'], formed by the oxidation of the above acid with potassium permanganate, crystallises in plates belonging to the monoclinic system; it melts at 70—71°, is sparingly soluble in water and petroleum, readily soluble in benzene and alcohol. Its aldehydic nature is evidenced by its ready reduction by silver salts, and the formation of a phenylhydrazine compound, $C_{16}H_{13}N_3$, crystallising in golden leaflets melting at 195—198°. The authors propose to extend these researches to other aldehydes and their derivatives. V. H. V.

Paraquinaldine-acrylic Acid. By W. v. Miller and F. Kinkelin (*Ber.*, **18**, 3234—3239). Paramidocinnamic acid was prepared by the action of 100 grams of 38 per cent. hydrochloric acid and 100 grams of tin on a warm alcoholic solution of 25 grams of ethyl paranitrocinnamate. The product was freed from tin and evaporated, when crystals of the hydrochloride separated. The yield is 75 per cent. of the theoretical.

Paraquinaldine-acrylic acid,

$$C_9NH_7MeCH{:}CH{\cdot}COOH\ [Me : C_2H_2{\cdot}COOH = 2' : 3],$$

is obtained by heating 50 grams of paramidocinnamic acid hydrochloride with 50 grams of concentrated hydrochloric acid and 40 grams of paraldehyde for two hours at 100°. The product is diluted with water, filtered and evaporated, and the hydrochloride so obtained treated with sodium acetate, which precipitates the free acid. It forms small needles, which melt at 240—250° with decomposition, but can be sublimed in part unchanged; it dissolves sparingly in water and cold alcohol, readily in dilute alkali solution. The *hydrochloride* (with 1 mol. H_2O) crystallises in prisms, readily soluble in water; the *nitrate* (with 1 mol. H_2O) forms colourless prisms with vitreous lustre. The *platinochloride*, $(C_{13}H_{11}NO_2)_2,H_2PtCl_6 + 2H_2O$, forms thick, reddish-yellow prisms.

Paraquinaldine-aldehyde, $C_9NH_5Me{\cdot}CHO$ [Me : CHO = 2' : 3], is prepared by oxidising the above compound with potassium permanganate at 0°. It crystallises from a mixture of benzene and light petroleum in yellowish plates melting at 106°, readily soluble in alcohol, ether, benzene, and in acids. The *platinochloride* (with 2 mols. H_2O) crystallises in orange-coloured prisms. The *phenylhydrazine compound* forms gold-coloured prisms which melt at 160°. When the aldehyde is heated for some hours at 150° with an equal quantity of quinaldine, a compound, $C_9NH_6{\cdot}CH{:}CH{\cdot}C_9NH_5Me$, is formed. It is a yellow powder, almost insoluble in the usual solvents, soluble in aniline, phenylhydrazine, &c., and in strong acetic acid.

N. H. M.

Derivatives of Isoquinoline. By S. Gabriel (*Ber.*, **18**, 3470—3480).—In continuation of investigations on substances derived from isobenzalphthalide (Abstr., 1885, 1231), the author adds further obser-

vations on *isobenzalphthalimidine*. This substance, to which the formula $C_6H_4<^{-CH\cdot CPh-}_{C(OH):N}>$ is now given in place of

$$C_6H_4<^{CH:CPh}_{-CO\cdot NH-}>,$$

crystallises in the asymmetric system with axial ratios $a:b:c = 0{\cdot}8601:1:(?)$; its formation from isobenzalphthalide is analogous to that of oxynicotinic from cumalinic acid. The presence of a hydroxyl-group in the compound is evidenced by the formation of a compound, $C_{15}H_{10}NCl$, from it by the action of phosphorus oxychloride, whilst phosphoric chloride yields a dichloro-compound, $C_6H_4<^{CCl:CPh}_{CCl=N}>$. The latter melts at 162—163°; the former crystallises in needles melting at 77—78°; it is soluble in benzene and ether.

On heating the dichloro-compound with amorphous phosphorus (1 part) and hydriodic acid (8 parts), a monochloro-compound, $C_{15}H_{10}NCl$, is produced, isomeric with the one above mentioned; it crystallises in short glistening pyramids, melts at 68—70°, and forms a crystalline hydrochloride, $C_{15}H_{10}NCl,HCl$, and a *platinochloride*, crystallising in sparingly soluble, orange-yellow needles; to this compound, the formula $C_6H_4<^{CCl:CPh}_{CH=N}>$ is ascribed. If these formulæ are correct, therefore, the constitution of the last-named substance is that of a phenylisoquinoline. The monochloro-compound (m. p. 77°), when heated with amorphous phosphorus and hydriodic acid, is converted into phenylisoquinoline, $C_6H_4<^{CH:CPh}_{CH=N}>$, which crystallises in rhombic plates melting at 103—105°; its *hydrochloride* forms orange-red pointed needles.

On reduction with sodium amalgam, both the di- and mono-chloro-derivatives yield tetrahydride of phenylisoquinoline, $C_{15}H_{15}N$, which forms glassy crystals; it melts at 45—48°, and is soluble in water and acetic acid. It is probable that phenylisoquinoline is identical with a base formerly obtained by the author by the distillation of phthalimide with zinc-dust. V. H. V.

Paraxanthine and Heteroxanthine. By G. Salomon (*Ber.*, **18**, 3406—3410).—As a correction of former observations on paraxanthine, a constituent of human urine (Abstr., 1883, 601), the author ascribes to it the formula $C_7H_8N_4O_2$, namely, that of a dimethylxanthine, isomeric with theobromine, instead of the more complex formula $C_{15}H_{17}N_9O_4$. Further, it is now shown that paraxanthine forms a sparingly soluble precipitate with mercuric chloride, provided that the latter be in excess; this consists of colourless prisms, melting with partial decomposition; it is readily soluble in hot water. Paraxanthine hydrochloride crystallises with difficulty; it forms an orange-yellow crystalline platinochloride.

These extended researches have led to the isolation of another constituent of human urine, which it is proposed to call *heteroxanthine*. In order to separate this, the amorphous residue obtained as a bye-

product in the preparation of paraxanthine, is dissolved in ammonia, the solution filtered from the calcium phosphate and oxalate, and evaporated down, when the heteroxanthine crystallises out. It is best purified by means of the crystalline sodium-derivative obtained by the addition of soda to a solution of the heteroxanthine. The base is a white, amorphous, granular powder; it exists in urine in the proportion of 1 gram in 1000 litres. Its composition is expressed by the formula $C_6H_6N_4O_2$, corresponding with that of a methylxanthine. It is differentiated from hypoxanthine, xanthine, and guanine by the above-mentioned soda reaction, and from paraxanthine by its amorphous form, its sparing solubility, the ready solubility of its hydrochloride, in not yielding a precipitate with picric acid in presence of hydrochloric acid, and in not emitting the characteristic odour of paraxanthine when heated. It is precipitated by copper acetate, phosphotungstic acid, and lead acetate in presence of ammonia. Its hydrochloride forms transparent crystals arranged in tufts; it gives a minutely crystalline platinochloride. With mercuric chloride, the base yields a greyish-yellow precipitate, becoming crystalline after a time; it contains chlorine, and is converted by silver nitrate and ammonia into a silver compound. V. H. V.

Doundaké or African Quinine. By E. Heckel and F. Schlagdenhauffen (*Ann. Chim. Phys.* [6], **6**, 313—328). The authors have made careful examinations of this bark from various sources, and, contrary to the results obtained by Bochefontaine, Feris, and Marcus, find that it contains no alkaloïd whatever, but that the bitter principle consists of two nitrogenous, resinoïd, yellow colouring matters, soluble in alcohol and alkalis, one being insoluble and the other soluble in water. The bark also contains a third principle of a brown colour, insoluble in water and having no taste; glucose and small quantities of tannin, chlorophyll, and two fatty substances were also present. A. P.

Strychnine-derivatives. By W. F. Loebisch and P. Schoop (*Monatsh. Chem.*, **6**, 844—862).—*Nitrostrychnine*, $NO_2{\cdot}C_{21}H_{21}N_2O_2$, may be obtained by gradually adding 1 part of anhydrous strychnine nitrate to 10 parts by weight of sulphuric acid, the temperature being kept below 20°, and the mixture allowed to remain for eight days, then poured into 80 parts of water and neutralised with ammonia, the nitro-compound thus precipitated is collected and recrystallised from dilute alcohol; it forms yellowish plates, becomes slightly brown, and melts at 225°, and dissolves in the usual solvents. The yield is about 88 per cent. of the strychnine nitrate employed. It is as strongly basic as strychnine, and does not give any colour reaction with sulphuric acid and dichromate. The *hydrochloride*,

$$NO_2{\cdot}C_{21}H_{21}N_2O_2,HCl$$

forms hair-like crystals, and is insoluble in cold alcohol. The *platinochloride*, $(NO_2{\cdot}C_{21}H_{21}N_2O_2)_2,H_2PtCl_6$, forms a light yellow granular precipitate, and is insoluble in water and alcohol; on dry distillation, it gives a strong quinoline-like odour. The *nitrate*,

tartrate, *oxalate*, and *acetate* were also prepared. Solutions of the acetate yield precipitates with the usual alkaloïdal reagents.

Amido-strychnine, $NH_2{\cdot}C_{21}H_{21}N_2O_2$, may be prepared by acting on the hydrochloric acid solution of the nitro-compound with tinfoil at about 20°; it forms small, colourless, cubical crystals, melts at 275°, and boils without decomposition at about 280° under 5 mm. pressure; it is insoluble in water, and acts as a diacid-base. Its salts are considerably more soluble in water than those of strychnine; on exposure to the air, they are coloured a reddish-violet, solutions of the neutral salts yield precipitates with the usual alkaloïdal reagents; by treating the base dissolved in excess of nitric, hydrochloric, or sulphuric acid, with a solution of potassium dichromate, an intense pure blue coloration, or in concentrated solutions even a blue precipitate, is formed, which if the free mineral acids be removed by the addition of sodium acetate, will remain unaltered for a week; by warming the solution in the presence of acid, it turns violet, and finally if the quantity of free acid is considerable, forms a clear yellow solution; the reaction is as delicate as the dichromate strychnine reaction. By heating the amido-base with alcoholic potash and chloroform, it yields the characteristic isonitrile odour. The *hydrochloride* $NH_2{\cdot}C_{21}H_{21}N_2O_2,HCl$, forms long, brilliant prisms, and is readily soluble in water; the *platinochloride* is rather unstable, and forms an amorphous, yellow precipitate, and by dry distillation yields a quinoline-like odour. The *nitrate* forms octohedra, and after a time turns a violet colour. By treating an alcoholic solution of the nitrostrychnine described above with alcoholic potash, the potassium-derivative of a compound isomeric with the nitro-compound, and to which the authors give the name of "*xanthostrychnol*," is formed; the free compound crystallises in slender yellow needles, is insoluble in water, but dissolves in most of the other usual solvents; it yields precipitates with the alkaloïdal reagents. The *platinochloride* $(C_{21}H_{21}N_3O_4)_2,H_2PtCl_6$, forms a bright-yellow precipitate; the *nitrate*, *sulphate*, and *hydrochloride* were also prepared. Although in the above compounds xanthostrychnol acts as a base, it also possesses acid or phenolic properties, yielding unstable compounds with bases. The *potassium*-derivative forms brilliant, ruby-red needles, is decomposed by carbonic acid, and is soluble in the usual solvents; when heated, it explodes slightly; its solution yields precipitates with most of the metallic salts, which are, however, very unstable. By acting on the hydrochloric acid solution of xanthostrychnol with tinfoil, two reduction products are formed, which are not yet thoroughly examined.

A *monobromstrychnine*, $C_{21}H_{21}BrN_2O_2$, which differs from that obtained by Beckurts (Abstr., 1885, 911), may be prepared by treating a sulphuric acid solution of strychnine with bromine, the acid solution is diluted, and the base precipitated with ammonia; it forms colourless needles, which dissolve readily in water, but are insoluble in alcohol; its solution in sulphuric acid yields an indigo-blue coloration on the addition of potassium dichromate; its salts are more soluble in water than the corresponding strychnine compounds; the hydrochloride, the nitrate, and the platinochloride were prepared.

Strychninesulphonic acid, $C_{21}H_{21}N_2O_2{\cdot}SO_3H$, may be prepared by slowly adding 1 part of anhydrous strychnine sulphate to 6 parts of fuming sulphuric acid, containing 30 per cent. of the anhydride, keeping the temperature below 20°, and allowing the mixture to remain for a fortnight. It forms a brittle, transparent, yellow mass, readily soluble in water and alcohol; it does not yield any coloration with sulphuric acid and potassium dichromate. The *barium*, *calcium*, *potassium*, *sodium*, and *lead* salts were prepared, they are all soluble in water. By fusing the acid with sodium hydroxide, a new derivative is formed which yields a violet colour with ferric chloride. The authors have repeated the experiments of Beckett and Wright (this Journ., 1874, 655), of Schützenberger (*Annalen*, **108**, 353) and of Shenstone (Trans., 1885, 141), but cannot confirm their results. An examination of the physiological action of nine derivatives of strychnine shows that they all possess poisonous properties, although in a less marked degree than strychnine itself. A. P.

Strychninesulphonic Acids. By C. Stoehr (*Ber.*, **18**, 3429—3432).—Strychnine when heated with concentrated sulphuric acid at 100°, yields a *monosulphonic* acid, $C_{21}H_{21}N_2O_2{\cdot}SO_3H$, a colourless substance, very sparingly soluble in water.

Its *potassium*, *sodium*, and *barium* salts are colourless precipitates; the *ammonium* salt is soluble in water, but undergoes decomposition when its solution is evaporated.

Concentrated sulphuric acid and sulphuric anhydride at 150° yield a *disulphonic* acid, $C_{21}H_{20}N_2O_2(SO_3H)_2$, a colourless amorphous substance, readily soluble in water, sparingly soluble in ether and benzene; its neutral *barium* salt crystallises in minute plates, the *barium hydrogen* salt is a pale-yellow, amorphous powder.

These results are not in exact accordance with the observations of Loebisch and Schoop (preceding Abstract). V. H. V.

Piperidine from Pentamethylenediamine. By A. Ladenburg (*Ber.*, **18**, 3100—3102, comp. this vol., p. 139).—18 grams of pentamethylenediamine hydrochloride were quickly distilled, and the product again distilled with aqueous potash solution. Much ammonia is formed. The distillate was treated with strong potash solution, shaken up several times with ether, and the base extracted from the ether with hydrochloric acid. The salt thus obtained was identified as piperidine hydrochloride; the yield was 8 grams.

N. H. M.

Hopeine. (*J. Pharm.* [5], **12**, 460—462.)—This crystallisable narcotic alkaloïd can only be obtained with difficulty, as most varieties of hops do not contain more than traces. It was first obtained from wild American hops. The investigations of Smith, Williamson, Myers, and Springmühl, show that the pure alkaloïd has an energetic action similar to that of morphine. German hops contain only traces of it; some English varieties have given 0·05 per cent., whilst American wild hops have yielded 0·15 per cent. In the pure form, it is obtained as brilliant white needles, or as a white, crystalline powder, soluble

in 800 parts of water at 15°, and in 50 parts alcohol at 15°; it crystallises out on cooling the hot alcoholic solution. To extract hopeine, hops are digested with a 16 per cent. solution of glucose containing a little acetic acid, then boiled for six hours under pressure. The liquid is filtered through carbon, and is evaporated until the sugar crystallises. The alkaloïd is extracted from the residue by means of alcohol, and the solution filtered and evaporated. The residue is treated with ether and alkali to separate certain alkaloïds present, and finally pure hopeine is obtained by repeated crystallisations of its alcoholic solutions. J. T.

New Acid Analogous to Cholic Acid. By P. Latschinoff (*Ber.*, **18**, 3039—3047).—Cholic acid obtained from ox-gall was found to contain a new acid, *choleic acid*, $C_{25}H_{42}O_4$, which was separated from it by means of the barium salt. The new acid forms large, quadratic crystals (with $1\frac{1}{2}$ mol. H_2O), but separates from a concentrated solution in groups of slender needles (anhydrous); it is less soluble in water, alcohol, and ether than cholic acid. The anhydrous acid melts at 185—190°. The *barium* (with 3 mols. H_2O) and the *silver* salts were prepared. When choleic acid is oxidised by means of potassium dichromate and sulphuric acid, it yields cholanic acid. Cholic acid, treated in the same way, yields bilianic acid. The author confirms the result of Hammarsten (Abstr., 1881, 625), who obtained dehydrocholic acid by gently oxidising cholic acid with chromic anhydride in acetic acid solution, and repeated the experiment with choleic acid, which yielded *dehydrocholeic acid*, $C_{25}H_{38}O_4$. This forms irregular plates, with a fatty lustre, melting at 182—183°. The salts are analogous to those of dehydrocholic acid, but are more sparingly soluble. N. H. M.

Digestion of Elastin with Pepsin. By J. Horbaczewski (*Chem. Centr.*, 1885, 843).—Elastin is slowly digested by gastric juice, with formation of hemielastin and elastinpeptone; these substances were obtained pure by dialysis. In aqueous solution, hemielastin is precipitated by acetic acid and potassium ferrocyanide, whilst elastinpeptone remains unprecipitated. Hemielastin, when dried for some time at 110—120°, becomes insoluble, and, with exception of microscopic structure, acquires all the properties of elastin; elastinpeptone contains more hydrogen and oxygen than elastin.

H. P. W.

Proteïds. By P. Schützenberger (*Compt. rend.*, **101**, 1267—1270).—Noncrystallisable leuceïn, obtained by the action of baryta on coagulated albumin, only gives analytical results concordant with the formula $xC_4H_7NO_2$ after drying for a long time at 140—150°. If dried at 100—110°, it retains water of constitution. Leuceïn can be split up into equal equivalents of two compounds. One is a strong acid, *proteic acid*, of the composition $C_8H_{14}N_2O_5$, which forms a gummy noncrystallisable barium salt insoluble in alcohol of 90°. The other, *glucoproteïn*, $C_8H_{16}N_2O_4$, is a neutral body, soluble in water and in cold absolute alcohol. It crystallises with difficulty in indistinct

crystals. These two compounds stand in the relation of an acid and the corresponding alcohol, and leucein dried at 150° represents the product of their union with liberation of water, thus: $C_8H_{14}N_2O_5 + C_8H_{16}N_2O_4 = H_2O + C_{16}H_{28}N_4O_8$ or $4C_4H_7NO_2$. These facts, combined with the author's previous researches (Abstr., 1879, 542) lead to the conclusion that albumin has the formula $C_{29}H_{48}N_8O_{10}$, and that its decomposition by baryta is represented by the equation $C_{29}H_{48}N_8O_{10} + 7H_2O = C_6H_{13}NO_2 + C_5H_{11}NO_2 + [C_8H_{14}N_2O_5 + C_8H_{16}N_2O_4] + H_2C_2O_4 + 2NH_3$, or one molecule of albumin is formed by the union of 1 mol. leucein with 1 mol. each of leucein, amidovaleric acid, and oxalic acid, and 2 mols. of ammonia, water being eliminated. This view agrees very closely both with the composition of albumin and the proportions of the products obtained by the action of baryta.

Leucein when oxidised, yields products which indicate that it is closely related to the succinic acid series. C. H. B.

Physiological Chemistry.

The Gastric Juices and the Histology of the Gastric Mucous Membrane of the Pig. By Ellenberger and V. Hoffmeister (*Bied. Centr.*, 1885, 673—674).—These researches are a continuation of those which the authors have already made on the horse. The gastric juice contains the same ferments as are found in the other domestic animals. It dissolves albumin, converting it into peptone, propeptone, and syntonin, coagulates milk, and decomposes fat, the latter even in large quantities. The pancreatic secretion contains more mucin, acid, and ferment than the secretions of the cæcum and pyloric region, whilst the extract from the regions of the gullet are free from ferment. The smallest amount of ferment is found in the cæcum. In the mucous membrane of the stomach, a diastatic ferment exists, and the extract of the pancreatic region coagulates alkaline or neutral milk, as does also the extract from the cardiac sac, but not so the pyloric extract—at least in a very imperfect manner. Lactic ferment has not been found, and none of the ferments are destroyed by freezing. E. W. P.

Animal and Vegetable Pepsin. By O. Schade (*Chem. Centr.*, 1885, 734—736 and 761—762).—The author has compared the digestive properties of pepsin with those of papayotin. The latter has no action on coagulated albumin in presence of hydrochloric acid, but effects a rapid digestion in weak alkaline solutions: thus 10 grams of the albumin, together with a 0·15 per cent. solution of potash, were completely dissolved when digested with 0·1 gram of papayotin at 40°. This ferment is also active in presence of certain organic acids, such

as lactic acid: but the alkali appears to be necessary for such sustained activity (compare *Pharm. Centr.*, **26**, 357). C. F. C.

Digestibility and Feeding Values of Cotton-cake and Meal. By H. Weiske and others (*Bied. Centr.*, 1885, 674—677).—The animals experimented on were South Down merino sheep, and the cake and meal were prepared from Egyptian seed from which the adhering cotton-fibres had been thoroughly removed. The chief differences in the composition of the two foods were in the nitrogenous matter and the oil; the meal containing 0·8 more nitrogen than the cake (more albumin, half as much amido-nitrogen, and about half as much nitrogen soluble in acetic acid and alcohol), whereas the oil was less by nearly 3 per cent. From the tables, which show the quantity of each food-constituent digested, it seems that all the constituents of the meal (oil excepted) are more easily digested than those of the cake, the nutrient ratio of the former being 1 : 1·4, of the latter 1 : 1·9. Comparing this food with rape-cake, which it resembles, it appears that in the meal there are 186·04 nutrient units, in the cake 175·10, and in the rape-cake 197·83 (albumin and oil ×5, non-nitrogenous matter and fibre ×1); taking 6·25 Marks per centner as the value of the meal, 6·00 M. for cake, and 6·75 M. as the value of rape-cake, the value per nutrient unit is 3·36, 3·42, and 3·41 pfennigs respectively, and to this value must be added the greater palatableness of the two first. E. W. P.

Estimation of the several Albuminoïds in Cow's Milk, and Influence of the Food on their Relative Proportions. By S. W. Parr (*Amer. Chem. J.*, **7**, 246—249).—The milk of a cow of common breed, about six years of age and six weeks in lactation, was analysed with the following average results, the caseïn being precipitated by acid, the albumin by boiling, and the "third albuminoïd" by tannic acid:—

Ration.	Hay, Indian meal, and bran.	Hay.	Hay, Indian meal, cotton-seed meal, and bran.
Caseïn	2·67	2·60	3·04
Albumin	0·46	0·33	0·46
Third albuminoïd and tannin	0·31	0·27	0·31
Total albuminoïds (Rittshausen's method)	3·08	2·86	3·37

H. B.

Physiological Action of Rosaniline Sulphate and Safranine. By P. Cazeneuve and R. Lépine (*Compt. rend.*, **101**, 1011—1012).—Rosaniline sulphate is entirely without physiological action, even in quantities of several grams, whether taken into the stomach or injected into the veins. Safranine, however, when injected into the veins of a dog, caused rapid acceleration and weakening of the heart's action, severe diarrhœa, and often albuminuria, ending in death. If administered through the stomach, diarrhœa was the only serious

result, the irritant action of the poison probably preventing its absorption. C. H. B.

Toxic Effect of Three Coal-tar Yellows. By P. Cazeneuve and R. Lépine (*Compt. rend.*, **101**, 1167—1169).—The authors have made experiments with three coal-tar yellows which are used somewhat largely for colouring confectionery and beverages, namely, *Manchester* or *Martius yellow* (dinitronaphthol yellow), *NS yellow*, a sulphonic derivative of the first colour, and *solid yellow*, a sulphonic derivative of amidoazo-orthotoluene. These were administered through the alimentary canal, or were injected into the veins. Manchester yellow even in small doses has a somewhat strong poisonous action, and produces vomiting, diarrhœa, panting respiration, and a high temperature, followed by death. NS yellow has no appreciable toxic action, and solid yellow is at least as innocuous. C. H. B.

Sparteïne Sulphate. By G. Sée (*Compt. rend.*, **101**, 1046—1048).—Sparteïne sulphate administered in solution strengthens the action of the heart and the pulse, and in this respect is equal to digitaline or convallamarine, whilst its tonic action is infinitely greater, more rapid, and more durable. It immediately regulates any disorder of the cardiac rhythm, and in this respect is far superior to any known medicine, and it resembles belladonna in accelerating the heart's action. These effects are produced in an hour, or at latest in a few hours, after the administration of the drug, and persist for three or four days after administration has ceased. C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

Respiration of Leaves in the Dark. By Dehérain and Maquenne (*Compt. rend.*, **101**, 1020—1023).—The ratio $\frac{CO_2}{O}$, determined by the vacuum method, already described, in the leaves of *Euonymus japonica*, *Pinus sylvestris*, and the Austrian pine, is sensibly lower at about 0° than at 35°. The retention of carbonic anhydride by the leaves of plants is due—in part at least—to the solution of this gas in the water which the leaves contain. C. H. B.

Variations in the Composition of the Gases in Leaves. By J. Peyrou (*Compt. rend.*, **101**, 1023—1024).—The proportion of free oxygen in the gas contained in leaves is always greater during the night than during the day, the mean difference being from 4 to 5 per cent., although sometimes it becomes as great as 8 to 10 per cent. The proportion of free oxygen is less in young leaves than in those fully developed, and less in the latter than in blanched leaves. It is also less in leaves which are exposed to bright light than in those which are in the shade. These results show that the proportion of free oxygen in the leaves increases when the activity of the protoplasm diminishes.

Experiments made on the same plant at different times of the day show that between 8 and 10 A.M. and between 4 and 5.30 P.M. the proportion of free oxygen is at a minimum, whilst at 11.30 A.M. to 2 P.M. it is at a maximum. The colour of the leaves is without influence on these results. C. H. B.

Methyl Alcohol in the Products of the Distillation of Plants with Water. By MAQUENNE (*Compt. rend.*, **101**, 1067—1069).—When fresh plants (*Euonymus japonica*, nettles, grass, ivy, maize, &c.) are distilled with water, the distillate contains methyl alcohol, which in the case of nettles amounts to about 0·3 per cent. of the weight of the dry plant. This alcohol may exist preformed in the plants, or it may be produced from some more complex substance during the process of distillation.

The essential oil of ivy has the composition $(C_{10}H_{16})_2,H_2O$, and is a terebenthene hydrate isomeric with terpinol. C. H. B.

Influence of Oxygen at High Pressure on the Disengagement of Carbonic Anhydride by Germinating Plants. By JOHANNSEN (*Ann. Agronom.*, **11**, 409—411; from *Untersuch. bot. Instit. Tubingen*, 1885, **1**, 686—717).—The general result of the experiments made with air and oxygen at the ordinary pressure, and at 2, 4, and 5 atmospheres, is that the disengagement of carbonic anhydride increases at first as the pressure of oxygen increases, but that this increase is only temporary; the respiration gradually diminishes (more quickly as the pressure is greater) and the plants rapidly die. The most interesting result of the experiments is the discovery of an inductive effect exercised by the presence of oxygen at a high pressure for a short time; as soon as the ordinary pressure is restored a great increase in the respiration is obtained amounting to as much as 50 per cent. in the case of maize. The cause of this inductive action is unknown. J. M. H. M.

Growth of Barley from Varieties of Seed. By MÄRCKER (*Bied. Centr.*, 1885, 696—704).—This paper is of local interest, its object being to show which is the best barley to grow in Saxony. In the second part the increase in albuminoïds is shown which is produced by the employment of Chili saltpetre; this increase may amount to 2·08 per cent. in the case of Moravian seed. E. W. P.

Composition of Maize. By K. PORTELE (*Landw. Versuchs-Stat.*, 1885, 241—262).—The first portion of this article is occupied by a description, accompanied by copious tables, of the composition of maize damaged by floods which occurred in the South Tyrol in 1882, and comparisons of this grain with others which had not been damaged. Another portion deals with the changes occurring during growth: they are as follows:—The percentage of water decreases whilst the dry matter increases; the percentages of ash, fat, nitrogenous matter, and starch regularly increase, but the increase of fat and nitrogenous matter is less rapid when the grain begins to harden. During the process of ripening, the sugar appears to exist both as

cane and fruit sugar, and so long as the grain remains soft, the quantity remains the same, but as soon as ripening sets in, then the sugar diminishes; and the principal increase in the hardened grain is in the extractive matter. The removal of the small flowers seems to have no influence on the ripening, neither does it appear that there is much change occasioned by the removal of the leaves.

E. W. P.

On Heated Hay. By E. Mach (*Landw. Versuchs-Stat.*, 1885, 263—270).—The following statements are the result of examination of hay which had been overheated in the stack. The samples analysed were in different stages of overheating, and were compared with some which had been unaltered. The dry matter was gradually reduced by one-third, the greatest reduction being in the crude fibre, then in the albuminoïds, and the least loss in the fat. These results are contrary to those obtained by E. Wolff, but the reason of this difference may be attributed to sampling. The percentage of fat in the charred hay seems to be higher than in the less altered hay, but this may be due to the solution of tarry (?) matters which were formed, and are soluble in ether. The last sample also contained a higher percentage of crude fibre than the others; this, with the increase of nitrogen and ash, is accounted for by the probable fact that the action of the heat was to render some of the cellulose and albuminoïds less soluble in alkalis and acid. Another remarkable fact noticed was that whereas in the first stages of heating the fibre was richer in hydrogen and carbon, but poorer in oxygen, the fibre of the charred hay was poorer in hydrogen but richer in oxygen; finally, the apparent increase of fibre was accompanied by a rapid decrease of non-nitrogenous extractive matter.

E. W. P.

Preservation of Sliced Beets in Silos. By G. Liebscher (*Bied. Centr.*, **14**, 757—764).—Having noticed certain discrepancies in the results of ensilage conducted according to favourite systems, the author made certain experiments, for doing which he possessed facilities, and gives the results in this paper.

He believes it quite possible to preserve sliced beetroots in silos with relatively little loss, but advises attention to the following points:—The silos should be either cemented or so well built that bottom moisture should not penetrate; silos constructed of earth he strongly condemns; the corners should be rounded off, and the silo should be very deep in comparison with its superficies. The process of filling should not occupy more than one or at most two days, and the closing should be quickly and securely done. The beets should be fresh and scrupulously clean, everything likely to cause fermentation carefully avoided, and if they are stored in summer, additional precautions against sun heat should be taken. With such precautions, the material will keep good for half or even a whole year, with extremely little loss.

J. F.

Absorption of Nitrogen by Cultivated Soils. By H. Joulie (*Compt. rend.*, **101**, 1008—1011).—The soils were contained in glass pots, furnished with lateral openings in the lower part, and standing

in glass crystallising dishes. 500 grams of broken glass were placed in the bottom of each pot, and on this 1500 grams of the soil free from manure. The soil was moistened with distilled water, the seeds introduced and the necessary moisture supplied by keeping the glass crystallising dish filled to a certain height with distilled water, which rose into the soil by capillary attraction. The pots were placed under a glass roof and surrounded by wire work, and were thus protected from rain and from birds. At the end of the season the crop was collected, dried, weighed, and analysed; the soil was also treated in the same way.

Two series of experiments were made. In one series, an argillo-siliceous soil from La Dombe was sown, the first year with buckwheat, and the second with rye-grass and mixed clover. In the second series, a non-argillaceous sand from Fontainebleau was sown with one crop of rye-grass. In every case, with the exception of one pot in each series, there was a distinct gain of nitrogen, which however varied between somewhat wide limits, amounting in one instance to as much as 0·577 gram per kilo. of soil.

The wide differences between the amounts of nitrogen absorbed by different pots indicates that it was not derived from nitrogen compounds in the air, since all the pots were exposed under the same conditions. It follows that it is the free nitrogen which has been absorbed.

The fact that the quantity of nitrogen absorbed is not proportional to the intensity of vegetation as measured by the weight of the crop produced, indicates that the absorption is not due to the processes of plant life. It may be due to the action of bacteria in the soils or in the water (compare Berthelot, this vol., p. 175). C. H. B.

Increase of Nitrogen in Grass Land. By P. P. Dehérain (*Compt. rend.*, **101**, 1273—1276).—An extensive series of analyses shows that whereas a field, which was cultivated with beetroot in 1875-6-7 and with maize for fodder in 1878, lost a large quantity of nitrogen, notwithstanding the application of manure, in 1879—1883, when it was sown with sainfoin, and in 1884-5, when it was allowed to remain as meadow, the proportion of nitrogen showed a decided increase, although no manure was applied since 1878. C. H. B.

Urinary Fermentation. By A. Müller (*Landw. Versuchs-Stat.*, 1885, 271—283).—After recapitulating what he has previously done in former years, the author proceeds to describe in full detail his latest work. Urine was mixed with a variety of compounds, and the mixture left to itself. The following are the results of the examination of the mixture after a considerable period had elapsed. As a rule, basic substances assisted, whilst acid compounds prevented fermentation. Neutral substances had their own specific action. Phosphoric acid does not have much influence; consequently it must be present in large quantities to produce any effect. Oxalic and acetic acids resemble sulphuric, nitric, and hydrochloric acids, but their action is of shorter duration, mildew in time being formed. Sulphurous anhydride has the most effect, not on account of its acidity, but because of

its antizymotic action by reason of its volatility and oxidisability, it can, however, only be employed in closed vessels. Chromic acid (as dichromate) is very energetic, but whether by reason of its high oxidising power or because of some specific action, is not yet ascertained. The manner in which oxidising agents act is still an open question. Potassium permanganate assists the fermentation, whilst potassium chlorate retards it. Bleaching powder counteracts any disposition to change, without causing any loss of ammonia by liberating nitrogen. The retarding action of alcohol is remarkable, being more effective than ether; but on account of its volatility, its action, like that of acetic acid, is not lasting. A mixture of borax and boric acid was not satisfactory, and lead oxide was less effectual than cupric oxide; on the other hand, barium chloride assisted fermentation. E. W. P.

Preservation of Farmyard Manure. By E. Heiden (*Bied. Centr.*, 1885, 662—666).—The object of these researches was to ascertain the change in the composition of manure after exposure in summer and winter, and under other conditions. When much salt was given to the cattle, no appreciable increase in dry matter was observed, although the quantity of urine voided was greater. By allowing the manure to lie heaped up for some weeks, there was a considerable loss in dry matter both during summer and winter; but by the addition of gypsum and superphosphate, this loss was greatly prevented. The latter compound also prevented loss of nitrogen, for, with this addition, only 6·0 per cent. was lost, whilst without it 22·2 per cent. of total nitrogen was lost. This was also found to be the case when the superphosphate was applied to the exposed manure, and further experiments showed that this material was vastly superior to kainit as a "fixant." E. W. P.

Employment in Agriculture of Phosphatic Slag from the Thomas Process. By M. Fleisher (*Bied. Centr.*, **14**, 738—756).—The supply of this bye-product being large, its employment as a manure would benefit both farmers and those who produce it. The author undertook an exhaustive examination of the subject, of which a *résumé* is given in this paper. As the mean of several analyses, it appears that the substance contains phosphoric acid 17·5 to 17·25, lime 48·29 to 49·6, magnesia 4·7 to 4·89, together with smaller quantities of iron, alumina, manganese, sulphur (free), sulphuric and silicic acids. The substance when at first removed is in fragments of irregular size, which fall into smaller pieces under the influence of the atmosphere, but they require to be ground finer for purposes of agriculture. Its appearance then is a brownish-black, coarse powder, containing numerous brilliant tabular crystals. It is sparingly soluble in water, more so in water charged with carbonic acid, as also in a solution of humic acid; whilst in acetic acid the whole of the phosphoric acid is dissolved. The author compares the solubility of several natural phosphates in these media, and shows that the ground slag is most easily attacked. Numerous experiments made at various experimental stations show very good results when the ground slag was tried against compounds of other manurial materials; and although

the author thinks it premature to give a definite opinion, he believes that there is a good future for the slag. He thinks that deep cultivation and mixture with the soil for tillage, and early top-dressing in the case of meadows is most desirable. J. F.

Analytical Chemistry.

Drying and Heating Apparatus. By V. Meyer (*Ber.*, **18**, 2999—3002).—The apparatus, of which a sketch is given, consists of a double-walled vessel supported on three feet; the inner space is of such a size as to hold an ordinary crucible. According to the temperature required a small quantity of water or other liquid having a constant boiling point is poured into the space between the walls of the vessel and heated to its boiling point, the vapour being condensed in a tube about half a metre long. The apparatus has the advantage over the usual air-bath that it saves the trouble of regulating the temperature; it also avoids the waste of gas. N. H. M.

Various Newly Proposed Indicators for Volumetric Analysis. By G. Lunge (*Ber.*, **18**, 3290—3291).—The author considers methyl-orange to be the best indicator. Will's tropæoline is less delicate; Fischer and Philipp's dimethylamidoazobenzene is also less delicate, and has no advantages over methyl-orange. Poirier's cotton-wool-blue (C4L) shows the change of colour from bright rose colour through violet to blue very sharply, but the change takes place before the alkali is completely neutralised. In the case of indigo sulphate the change of colour is only gradual.

N. H. M.

Quantity of Moisture remaining in a Gas dried by Sulphuric Acid. By E. W. Morley (*Zeit. anal. Chem.*, **24**, 533—542).—The method employed consisted in drying air of ordinary pressure by passage through strong sulphuric acid, and then passing it through a bulb apparatus, in which it first took up some moisture from diluted acid, was then largely expanded by reduction of pressure, and lastly again traversed strong acid (sp. gr. 1·8381). Now, since the tension of water vapour would be identical in the air at both pressures, more moisture would escape absorption in the second drying than in the first, and there would consequently be on the whole a loss of weight. The actual amount of loss observed indicates that the quantity of water remaining in the dried air is about 0·002 milligram per litre. This result closely agrees with that of Dibbits, who found that 308 litres of air, dried by sulphuric acid, gave up 0·7 milligram of water to phosphoric anhydride. M. J. S.

New Applications of the Nitrometer. By A. H. Allen (*J. Soc. Chem. Ind.*, **4**, 178—182).—Hitherto mercury appears to have been regarded as the only liquid with which the nitrometer could be filled,

probably owing to the fact that in estimating nitrates by the nitrometer the mercury itself takes part in the reaction. It is shown that for many purposes the mercury can be conveniently replaced by a dense aqueous liquid, saturated brine being most generally suitable. The following are some of the applications to which the nitrometer has been put when filled with such a liquid. In experimenting on Dott's method for estimating ethyl nitrite in "spirit of nitrous ether" and kindred preparations, the author instead of titrating the iodine liberated, proposes measuring the nitric oxide evolved by the use of the nitrometer. Good results are obtained also with the nitrometer method in estimating commercial sodium nitrite. 1 c.c. of NO at the ordinary conditions of pressure and temperature corresponds with 0·003184 gram of ethyl nitrite, hence 5 c.c. of samples of spirit of nitrous ether of reasonably good quality evolve from 25 to 40 c.c. of nitric oxide. Another useful application of the nitrometer is for the estimation of urea in urine. For the estimation of the amount of oxygen in commercial hydrogen peroxide, the author employs the nitrometer, operating as follows:—The instrument is filled with a saturated solution of sodium or magnesium sulphate, 1 c.c. of the sample is then introduced through the tap, and this is followed by a strong solution of potassium permanganate previously acidulated with sulphuric acid. The reaction occurs very promptly, and the permanent coloration of the contents of the tube suffices to show that an excess of the permanganate has been employed. When acidified potassium permanganate is used, the following reaction occurs:—

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

If an acidified solution of potassium dichromate is employed the results are sensibly lower than those obtained with potassium permanganate. Whilst the nitrometer is largely used as an instrument for evolving or measuring gases, it has not been applied to the absorption of gases. By the aid of two Lunge's nitrometers having their three-way taps joined by a short piece of india-rubber tubing, an apparatus for gas analysis is obtained capable of a variety of applications. The author has devised a simple apparatus for making analyses of blast furnace and Siemens' furnace gases, combining the various advantages of the instruments of Stead, Bunte, and Elliott. The apparatus is described in detail in the original paper, accompanied by drawings and full particulars in regard to the mode of procedure.

D. B.

New Qualitative Methods. By F. A. Holton (*Amer. Chem. J.*, **7**, 249—250).—*Separation of Iodine and Bromine.*—The solution to be tested is treated with dilute nitric acid, a very little dichromate of potassium and carbon bisulphide. The whole is filtered, and in the filtrate the bromine is liberated by chlorine-water. The same reaction may be employed to detect a chromate. H. B.

Estimation of Sulphur in Pyrites. By J. Clark (*J. Soc. Chem. Ind.*, **4**, 329—331).—Some time ago, Fahlberg and Iles (Abstr., 1878, 1005) showed that when sulphides are fused with caustic potash or caustic soda, the sulphur is completely converted into alkaline

sulphite or a mixture of sulphite and sulphate, provided that at least 25 parts of alkali are used for each part of sulphur, and they pointed out that under these conditions no sulphide or thiosulphate is produced. The author has recently found that when the alkali is intimately mixed with calcined magnesia, the sulphur under favourable conditions can be completely converted into sulphuric acid or alkaline sulphate with little more than the theoretical quantity of alkali, but it is always advisable to use a moderate excess. A new method for estimating the sulphur in pyrites has been based on this action. The process is described in detail in the paper. The results obtained are somewhat higher (about 0·5 per cent.) than by the wet process, owing to the fact that this process avoids the sources of error due to the presence of nitrates, iron, and excess of free acid, which so often lead to discrepancies. D. B.

Clark's Process for Estimating Sulphur in Pyrites. By G. LUNGE (*J. Soc. Chem. Ind.*, **4**, 449).—In criticising the process described in the preceding Abstract, the author states that his main reason for rejecting this and other dry processes for estimating sulphur in pyrites is that in this way the sulphur of galena (which is nearly always present) and of the sulphates of barium and calcium is estimated, none of which is of value to the consumer of pyrites, whilst by the wet process nearly the whole of that useless sulphur is left behind in the insoluble residue. D. B.

Use of Sodium Bromate in Volumetric Analysis. By KRATSCHMER (*Zeit. anal. Chem.*, **24**, 546—548).—This salt is easily obtained pure and dry, as it crystallises well and bears a heat of 180°; it liberates iodine exactly equivalent to the oxygen it contains, when it is added to an excess of an acidified solution of potassium iodide. It can therefore be used for standardising sodium thiosulphate. M. J. S.

Modified Molybdate Method for Estimating Phosphorus in Steel. By E. F. WOOD (*Chem. News*, **52**, 279—280).—The following process has been found efficient for the estimation of phosphorus in steel. The steel is dissolved in strong nitric acid, sp. gr. 1·20; the solution is concentrated to about half bulk, mixed with about an equal volume of a solution containing 50 grams of chromic acid dissolved in 1 litre of nitric acid, sp. gr. 1·420, and again boiled down to about half bulk. After this treatment, molybdic acid solution precipitates the phosphorus completely in about 20 minutes, both solutions being at between 30—40°. Determinations by this method take about 85 minutes. Aqueous solutions of chromic acid cannot be used with safety; therefore the process cannot be employed for pig-iron, inasmuch as strong nitric acid precipitates the silica in a very inconvenient form. D. A. L.

New Method for Estimating Phosphorus in Iron and Steel. By W. KALMANN (*Monatsh. Chem.*, **6**, 818—820).—1 to 10 grams of the sample are mixed with about double the quantity of a mixture of ignited magnesia and sodium carbonate, and the whole heated in a

platinum dish over a Bunsen burner for an hour, with constant stirring; after cooling, the powdered mass is treated with excess of a hot aqueous solution of citric acid, the whole filtered, and the filter well washed with a 1 per cent. solution of citric acid. The filtrate then contains all the phosphorus as magnesium phosphate, which is precipitated as ammonium magnesium phosphate by the addition of ammonium chloride and ammonia; this is filtered off, washed, redissolved, precipitated again, and finally weighed as pyrophosphate of magnesium; the method is very accurate, rapid, and convenient, yielding results practically identical with those obtained by the molybdenum method. A. P.

Separation of Zinc from Cadmium by Electrolysis. By S. Eliasberg (*Zeit. anal. Chem.*, **24**, 548—551).—The method published by Iver (*Bull. Soc. Chim.*, **34**, 18), in which the acetates are electrolysed, gives good results if the solution is kept hot and a current evolving 0·5—0·6 c.c. of detonating gas per minute, is maintained for six hours. The current from two Daniell cells, as prescribed by Iver, is not strong enough. Sometimes, however, zinc oxide separates at the edge, and spoils the operation.

The author prefers to use the double oxalates. The hydrochloric acid solution of the metals is evaporated to dryness, made up to about 100 c.c. with addition of 8—10 grams of potassium oxalate and 2—3 grams of ammonium oxalate, heated nearly to boiling and kept hot whilst electrolysed. The current is of such strength as to evolve 0·1—0·15 c.c. of detonating gas per minute. In 6 to 7 hours 0·15 gram of cadmium can be completely precipitated. M. J. S.

New Method for the Determination of Alumina. By K. J. Bayer (*Zeit. anal. Chem.*, **24**, 542—546).—The acid alumina solution is mixed with sufficient soda to redissolve the precipitated alumina. It is then divided and equal portions titrated with sulphuric acid, using in one case litmus, in the other tropæolin, as indicator. With litmus, the reddening commences as soon as the excess of soda and that in the form of aluminate are neutralised. With tropæolin, an additional quantity of acid, being that required to convert the alumina into $Al_2(SO_4)_3$, is required before the change from yellow to orange begins. The titration with tropæolin is best performed in a porcelain basin, using not more than 50 c.c. of liquid and 0·5 c.c. of tropæolin solution (1—1000), with a similar quantity of water and tropæolin in a second basin for comparison. Warming should be avoided, and the acid should finally be added in excess, and the excess titrated back with normal alkali.

Metals whose oxides are soluble in soda must first be removed. Bases precipitated by soda can be filtered off before titrating. Alkaline silicates are without influence.

In crude aluminate liquors, the method gives lower and more correct results than simple precipitation with ammonia and weighing, as in the latter case various impurities are precipitated at the same time.

M. J. S.

Volumetric Method for the Estimation of Alumina. By R. W. Atkinson (*Chem. News*, **52**, 311).—Phenolphthaleïn is recommended as superior to litmus in the first stage of K. J. Bayer's method for the estimation of alumina (preceding Abstract), whilst to be certain of the end point in the second stage, an alkaline solution tinged with the requisite quantity of tropæolin should always be used for comparison. D. A. L.

Estimation of Resin Oils in Mineral Oils. By H. Demski and J. Morawski (*Dingl. polyt. J.*, **258**, 82—87).—Valenta (Abstr., 1885, 93) has recently published a series of reactions by which adulterations of mineral oils with resin oils are detected qualitatively. These were based on the dextrorotatory power of resin oils, their greater solubility in glacial acetic acid at a temperature of 50°, and the higher iodine number obtained with resin oils (estimated according to Hübl's method). The authors have tested these reactions, their object being to ascertain whether they are suitable for quantitative determinations. Failing in this respect, it was found that by the difference in the solubility of resin oils and mineral oils in acetone, it was possible to obtain quantitative results. Resin oils are miscible in all proportions with acetone, whilst for the solution of mineral oils the use of several volumes of acetone is required. It was ascertained, however, by experiment that different mineral oils when adulterated with the same quantity of resin oil gave different solubility values with acetone. The original paper contains tables showing the solubility of the most important mineral oils in acetone and their behaviour therewith when mixed with known quantities of resin oils. D. B.

Kjeldahl's Method for the Determination of Nitrogen. By H. B. Yardley (*Chem. News*, **52**, 220).—The author has observed that when wool-dust is heated with chamber acid some free nitrogen is evolved. D. A. L.

Estimation of Water in Glucoses, Honey, &c. By H. W. Wiley and F. V. Broadbent (*Chem. News*, **52**, 280—281).—The substance, dissolved in 80 per cent. alcohol, is mixed with sand, dried for half to one hour, then treated with absolute alcohol, and dried until the weight is constant. For drying, a special form of oven is employed, which is heated by means of steam-pipes fitted with automatic valves and with traps, so that a uniform temperature is obtained. The whole is placed on lead supports in a leaden box containing sulphuric acid and pumice. D. A. L.

Adulteration of Honey with Sugars. By H. Hager (*Chem. Centr.*, 1885, 764—766).—The author gives the following qualitative tests for the presence of starch-sugar and cane-sugar as adulterants of honey. To detect the former, the honey is diluted with 3 vols. of water and filtered: 4 c.c. is introduced into a small test-tube, 6 drops of a 10 per cent. solution of mercuric nitrate is added, and, after shaking, 4 c.c. of absolute alcohol. On standing at the ordinary temperature, a precipitate gradually forms, if the honey contain a considerable

proportion of the sugar; with small proportions, the solution becomes opaque, but no precipitate is formed. More simply, the honey diluted as above is introduced into a test-tube and absolute alcohol is added so as to form an upper stratum; the development of a milky opacity at the line of contact indicates the presence of the sugar. The presence of cane-sugar is detected by pouring the diluted honey upon concentrated sulphuric acid: at the line of contact browning takes place gradually, and in the course of an hour an opaque black stratum is formed. The reactions with honey free from such adulteration are very different: the observer requires to familiarise himself with these differences by blank experiments.

Evidence of the genuineness of a honey is afforded by the presence of pollen grains, which may be easily identified by examination under the microscope. When magnified to 100 to 200 diameters the field should present from 5 to 10 of these grains (compare *Pharm. Centr.*, **26**, 327). C. F. C.

Salt Solutions as indicating the Richness of Sugar Beets. By Marek (*Bied. Centr.*, **14**, 780—782).—It is a usual practice in Germany to estimate the value of beets according to their specific gravity, as found by floating sections of the root in solutions of salt of various densities; doubts as to the correctness of the method induced the author to examine it; his opinion is that it is quite untrustworthy. J. F.

Determination of Fat in Milk. By G. C. Caldwell and S. W. Parr (*Amer. Chem. J.*, **7**, 238—246).—The accuracy of Marchand de Fecamp's method has been many times called into question, the results frequently differing from the gravimetric estimation by 0·3 to 1·0 per cent. The addition of a few drops of caustic soda, or better still ammonia solution, before treatment of the milk with ether is in some cases essential, and in no case is it hurtful. Instead of a straight graduated tube closed at one end, the authors use a tube open at both ends, the upper and graduated portion of which is narrow so as to allow of more accurate reading; the wide end is closed by a cork; such a tube is very easily cleaned. The proportions of ether, alcohol, and water (of the milk) necessary for the formation of a layer of ether containing all the fat are 75 : 100 : 135. H. B.

Butter Analysis. By A. Andouard (*J. Pharm.* [5], **12**, 453—455).—In analysing a sample of butter, the amount of fixed fatty acids insoluble in water is determined by Hehner and Angell's method, and afterwards the amount of volatile fatty acids soluble in water by Lechartier's method (*Ann. Agronom.*, **1**, 456), as modified by Reichert (Abstr., 1879, 406) and Schmitt (Abstr., 1884, 268). The fixed fatty acids have been found by various experimenters to vary from 85 50 to 89·95 per cent. For the volatile acids, 2·5 grams of butter ought to give on distillation a solution requiring 13—15 c.c. of decinormal soda solution. The purity of a sample of butter from Brittany was questioned, as the fixed acids amounted to 89·30 per cent. On examination, five samples of known purity gave 88·86—89·30; and the volatile acids required for saturation, 13·00 c.c. decinormal soda solu-

tion (= 4·58 per cent. butyric acid) to 14·50 c.c. (= 5·10 per cent. butyric acid). These figures show that butter from that district may be pure although it contains over 89 per cent. of fixed fatty acids.

J. T.

Examination of Commercial Copaiba Balsam. By E. Praël (*Arch. Pharm.* [3], **23**, 735—754, 769—779).—The author has examined 15 samples of copaiba balsam, and gives the results in tabular form, showing the physical characteristics of the samples and their behaviour with various solvents. He then considers the various methods of adulterating copaiba balsam. The sp. gr. varied from 0·916 (Para) to 1·009 (Angostura raw), or omitting the last, which might contain water, 0·995 (Maracaibo). The amount of resin varied from 23·87 per cent. (Para) to 61·43 per cent. (Maracaibo). The sp. gr. of the ethereal oil yielded by the samples was 0·897—0·908 (Para and Bahia respectively). All varieties gave clear solutions with carbon bisulphide, chloroform, amyl alcohol, and benzene. Absolute alcohol gave a slight turbidity in three cases; this usually indicates the presence of a fatty oil (other than castor-oil); still the samples in question appeared to be free from such oils. With chemical reagents the results obtained agreed generally with those given by Hirschsohn (*Arch. Pharm.*, **211**, 162 and 177).

Adulteration with fatty oils, with Gurjun balsam, turpentine oil, sassafras oil, colophony, and similar resins is also discussed by the author. To detect colophony, he recommends powdering 2 grams of the residue left on heating the balsam over a water-bath, and stirring vigorously with 10 times its weight of 70 per cent. alcohol; after an hour, it is filtered, and the filtrate treated with a gentle current of hydrogen chloride for half an hour. No yellow resinous precipitate should appear.

J. T.

Separation of Picrotoxin from its Solutions. By R. Palm (*Zeit. anal. Chem.*, **24**, 556—559).—On a former occasion (*ibid.*, **22**, 274) the author proposed the use of lead acetate and alcoholic ammonia for the precipitation of picrotoxin. He now finds that a decomposition of the picrotoxin by the ammonia takes place, and that organic matters, not having a bitter taste and not giving the reactions of picrotoxin, remain in solution. Carbonate of ammonia has a similar action.

If, however, a picrotoxin solution (aqueous or alcoholic) is vigorously shaken with lead hydroxide, freshly precipitated from the acetate by ammonia, and thoroughly washed, every trace of organic matter is removed from the solution, and the precipitate gives, with cold sulphuric acid, the saffron-yellow colour, changing to reddish-violet on warming, which is characteristic of picrotoxin. On treating the precipitate with hydrogen sulphide, the picrotoxin is again obtained in solution (alcoholic by preference) and can be weighed after evaporation.

Digitaline and solanine are also removed from their solutions by lead hydroxide. The compound of the former gives with strong sulphuric acid a pale fawn colour, passing on addition of bromine or potassium bromide into emerald-green; that of the latter gives with

sulphuric acid a dark fawn colour, changing on addition of sugar to violet and then blue.

Bismuth hydroxide does not remove picrotoxin from its solutions. M. J. S.

Estimation of Tannin. By B. Hunt (*J. Soc. Chem. Ind.*, **4**, 263).—Procter (*ibid.*, **3**, 82), in order to precipitate the tannin, adds to 50 c.c. of the tannin solution 28·6 c.c. of gelatin solution and 10 c.c. of dilute sulphuric acid. He then saturates the liquid with salt, adds a little kaolin, and shakes thoroughly. All the tannin and almost all the gelatin are thus precipitated, and on filtering a clear bright solution is obtained. The author finds, however, that in order to obtain a clear filtrate free from tannin, it is not necessary to saturate the liquid with salt, and that in the case of materials containing any considerable quantity of gallic acid, the results are too high, owing to the precipitation of some of the gallic acid. He therefore proposes to operate as follows:—50 c.c. of the tannin solution is run into a small dry flask; to this 25 c.c. of a freshly filtered solution of gelatin (2 grams per 100 c.c.) is added. The flask is then shaken, 25 c.c. of a saturated solution of salt containing 50 c.c. of strong sulphuric acid per litre is now added, together with a small quantity of pure kaolin or barium sulphate. The solution filters easily and quickly, and gives a clear and bright filtrate. D. B.

Reaction of Atropine and related Alkaloïds. By A. W. Gerrard (*Zeit. anal. Chem.*, **24**, 601; and *Chemiker Zeitung*, **8**, 457).—An alcoholic solution of atropine, when boiled with an aqueous solution of mercuric chloride, throws down mercuric oxide, and with the excess of mercuric chloride forms a double salt,

$$C_{17}H_{23}NO_3,HCl,2HgCl_2,$$

which on cooling separates in tufts of small foliated crystals. The presence of water is essential.

A similar reaction is given by hyoscyamine, daturine, duboisine, and homatropine, but by no other alkaloïds. M. J. S.

Uranyl Acetate as a Reagent for Albumin. By N. Kowalewsky (*Zeit. anal. Chem.*, **24**, 551—556).—The albumin of blood serum and of white of egg is completely precipitated by a small excess of uranyl acetate. A solution containing as little as 0·019 per cent. of albumin gives distinct flocks with this reagent, the sensitiveness of which as a test for albumin is only exceeded by that of trichloracetic acid. On mixing 5 c.c. of a 10 per cent. solution of dog's blood serum with 0·00486 gram of the uranium salt, the filtrate is perfectly free from both albumin and uranium. The precipitate is somewhat soluble in water, less so in presence of excess of uranyl acetate, and can be washed with alcohol. It is readily soluble in dilute acetic (2 per cent.), sulphuric (1 per cent.), hydrochloric, nitric, formic, lactic, tartaric, and citric acids, but not in carbonic anhydride or boric, arsenious, picric, or salicylic acids. It is decomposed by alkalis or alkaline carbonates with precipitation of alkaline uranates. Its solution in dilute nitric acid becomes turbid when mixed with strong nitric acid; that in

acetic acid yields a precipitate when neutralised. Its solubility in acetic acid affords a means of separating it from uranyl phosphate.

In five experiments, one part of albumin (determined by precipitation with alcohol) gave from 111·3 to 131·4 parts of the uranium compound, containing from 12·09 to 13·4 per cent. of ash (Ur_3O_8).

A similar precipitate is produced by this reagent in the serous fluid of the pericardium, the aqueous humour, and the liquid expressed from the crystalline lens.

Since normal as well as albuminous urine yields a precipitate, it is necessary to identify the latter by dissolving the precipitate in dilute nitric acid, and testing this solution with the concentrated acid.

M. J. S.

Technical Chemistry.

Micro-organisms in Potable Water. By T. Leoni (*Gazzetta*, **15**, 385—392).—In this paper an account is given of experiments on micro-organisms in potable water by Koch's gelatin cultivation method. The Monaco water supply from the Maugfall spring was selected as a type of pure water; as supplied to the city, it contains five micro-organisms per 1 c.c. After remaining in sterilised vessels for 24 hours, it contains more than 100, after four days 315,000, increasing to more than one million per c.c. at the end of a month, and from this gradually decreasing to 95 after six months. A similar increase of micro-organisms has been observed by Cramer in a report to the Water Commission of the City of Zurich. It is further noticed that in water containing carbonic anhydride, whether from artificial or natural sources, the micro-organisms do not increase; and by a series of comparative experiments, it is shown that the result is due solely to the carbonic anhydride, not to the action of pressure or diminution in the proportion of oxygen.

V. H. V.

Purification of Sewage Water. By J. König (*Bied. Centr.*, **14**, 721—738).—Differences of opinion exist as to when foul water should be considered purified, some persons thinking the removal of visible impurities sufficient, although organic matters of a highly noxious character may remain in solution. The author has studied various systems of purification, and reviews many of them in the present paper. As compared with other systems, he considers irrigation the method most nearly approaching nature, and cites English experiences as given in the evidence before the Rivers Pollution Commission, and experiments with the sewage of Berlin and Breslau. Tables are given containing analyses of the sewage and effluent waters, and the crops grown on the irrigated fields are noted. The author believes that the removal of mineral impurities is largely influenced by the nature of the crop and its requirements, and that the power of the soil to absorb impurities is limited, being mainly dependent on its

physical condition, porosity, free access of air, &c. Thus a poor, light, sandy soil is more suitable for such purposes than a close, heavy one, the organic impurities being quickly oxidised to harmless compounds in the former.

Filtration methods, whether through earth, sand, or peat, are considered to be far inferior to irrigation. The action is simply mechanical, and only removes visible impurities.

Of purification by chemical means, the author says there are 22 systems, the employment of lime being a feature of nearly all, and all of them depending on the formation of an insoluble precipitate, which in subsiding carries down with it other matters. It was found in all such cases that the dissolved organic impurities of the sewage were not removed, although the water appeared clear. Some of those methods include the passing of carbonic anhydride through the water, after addition of lime and alum.

Certain experiments of the author bear on the so-called self-purification of rivers, acting on the fact that water possesses the power of rapidly absorbing oxygen when presented to it in the state of spray or a thin layer. The author had an apparatus constructed of finely perforated metal, over which he caused a stream of water to flow, most of it descending in fine rain and being largely in contact with the air. Ordinary potable as well as sewage waters were experimented with, and the results were very satisfactory, the oxygen absorbed being considerable in amount. It is recommended that when sewage water is discharged into rivers, such should be chosen as have a long course and a rapid flow, presenting considerable surface to the atmosphere.

The author describes an arrangement of his own for partially disinfecting the waste water of factories. He forces the chimney gases through the water, to which lime has been added; the carbonic anhydride precipitates the lime, whilst the creosote and such matters attack the organic impurities. J. F.

Purification by Irrigation of Water flowing from Factories. By J. König and C. Böhmer (*Bied. Centr.*, 1885, 659—662).—Water which is contaminated with sewage loses much of its dissolved oxygen, which is, however, recovered by causing it to flow over the soil; at the same time the dissolved organic matter is reduced by $\frac{1}{10}$ to $\frac{1}{3}$. This organic matter is partly absorbed by, partly oxidised in the soil; this is also the case with the ammonia and organic nitrogen. As regards experiments made with water from a straw-paper factory, where the water was first mixed with lime, and allowed to settle in tanks, it was found that the organic matter was reduced in the tanks to $\frac{1}{3}$, and on the field to $\frac{1}{4}$; the oxygen in the water in the tanks was also reduced, but was recovered by irrigation. The increase in potash was due to solution from the straw; an increase in ammonia was observed in the water on the fields, due to decomposition of the organic nitrogen; nitrates were transformed into nitrites and phosphates precipitated by the lime. To purify such water to the utmost, the extent of land must be large and the soil be open.

E. W. P.

Obtaining Sulphur from Furnace Gases. By E. Hänisch and M. Schröder (*Dingl. polyt. J.*, **258**, 225).—The object of the process patented by the authors is to reduce the sulphurous anhydride contained in furnace gases to sulphur by passing the gas over coal heated to redness. According to a second process, the sulphurous anhydride is reduced by mixing it with twice the quantity of carbonic oxide, according to the equation $SO_2 + 2CO = 2CO_2 + S$.

D. B.

Utilisation of Alkali Waste. By E. W. Parnell and J. Simpson (*Dingl. polyt. J.*, **258**, 287).—The residuary ammonium chloride liquors from the ammonia-soda process are heated with soda waste from the Leblanc process in a closed vessel, whereby calcium chloride is formed and ammonium sulphide given off with the steam. This is absorbed in water and employed for the manufacture of sodium carbonate by being conducted into a solution of sodium chloride, together with carbonic anhydride, in the same manner as free ammonia is used in the ordinary manufacture of sodium carbonate by the ammonia-soda process. The sulphur is separated as sulphuretted hydrogen, and after washing with an acid solution, may be burnt or dealt with by any of the known methods for obtaining sulphur.

D. B.

Alumina in Superphosphate. By H. B. Yardley (*J. Soc. Chem. Ind.*, **4**, 386).—In a previous communication (*ibid.*, **3**, 430), the author proved that if a sufficient amount of free acid is present in superphosphate no reduction takes place from the presence of alumina. It having been suggested that the interval of one month between the tests of the mixture was insufficient, the experimental samples were retested nine months after making, the results confirming the original conclusion arrived at by the author. D. B.

The Jameson Coking Process. By J. Jameson (*J. Soc. Chem. Ind.*, **4**, 314—316).—After working this process successfully for some time, mechanical difficulties arose and defects were discovered necessitating the introduction of several modifications. In the present paper, the author refers to the improvements which have been practically applied. The first and great cause of all troubles was proved to be ingress of air at the oven bottom, its effect being to decompose the ammonia and the oil on coming into contact with the warm gases from the oven. To overcome this difficulty it is proposed to examine the tightness of the oven bottom from time to time. Experiments are still in progress with a view to discover the best and cheapest means of making a perfectly air-tight bottom. One important element in the success of the process appears to be the construction of the oven floor; the best floor in the author's judgment being one formed of alternate fire-bricks and T-irons, the bricks being shaped so as to take in the T-iron and form a level floor. The author in the next place refers to an improvement in partially cooling the gas of each oven separately before passing into the main. Gas and products of different constitution coming off at different periods of the process, it may happen that hot gases from an exhausted oven mix with rich gases from a half-burned oven, in which case the products in the

latter would be decomposed. With cooled gases, however, this action is prevented. Finally, it is recommended to condense the steam used for the steam-jet so as to recover the oil and ammonia brought down by the steam, and simultaneously utilise the gas for burning purposes. D. B.

Wood Naphtha. By C. A. Fawsitt (*J. Soc. Chem. Ind.*, **4**, 319—321).—After referring to the composition of wood, the author discusses the conditions on which the yield of the different products of wood distillation depends. The species, age, and condition of the wood, as well as the soil it is grown in, affect the yield of the different products. Hard woods are preferred by the wood distiller, oak, beech, and birch being mostly used. The following particulars show the difference in yield of acid for 100 parts of oak and Scotch fir :—

	Crude acid.	Acetic acid.	Tar.	Charcoal.
Oak.....	47·6	5·4	6·4	24·9
Scotch fir....	45·0	2·7	10 0	28·0

The yield of products is influenced also by the temperature, size, and shape of the retorts. As a rule, a low heat gives more charcoal, acid, naphtha, and tar, but less permanent gas than a high temperature. The aim of the distiller being to obtain the largest possible yield of acid, the heat of the retort is regulated accordingly. It has been found that the most suitable temperature is 350—400°.

In the second part of the paper, the author refers to the preparation, properties, and uses of wood-naphtha. The crude naphtha has a sp. gr. varying from 0·970 to 0·990. It has a dark brown colour and strong odour. Besides water, it contains methyl alcohol, acetone, methyl acetate, aldehyde, allyl alcohol, dimethyl ethylidine ether, also small quantities of mono-, di-, and tri-methylamine, ammonium acetate, oils, and tarry matter. As to the methods in use for working up the crude naphtha, that involving distillation by means of lime gives the best product. The lime retains the water and acid, almost entirely decomposes the methyl acetate and simple and compound ammonias, converts the greater part of the oils into solid resinous bodies of high boiling points, and diminishes the percentage of acetone, which, on treatment with lime, gives condensation-products of high boiling point. In conclusion, the author refers to the composition of the oils present in the crude naphtha. D. B.

Maple Sugar Industry in the United States. By H. W. Wiley (*Ann. Agronom.*, **11**, 392—404).—Sucrose is almost the only sugar contained in the sap of the sugar maple (*Acer saccharinum*) ; the percentage varies under different circumstances from 1·95—3·5, exceptionally 4·30 has been found. Samples of maple sugar show generally more than 80 per cent. of saccharose. The sap contains 0·0088—0·0103 per cent. albuminoïds; no starch; acid equal to 0·0005—0·005 per cent. malic acid; ash 0·146 per cent. A very little glucose is found towards the end of the season. The addition of alcohol precipitates a little gum. The remainder of the paper relates to details of cultivation, &c. J. M. H. M.

Preparation of Acids from Hydrocarbons. By E. Schaal (*Dingl. polyt. J.*, **258**, 230).—For the conversion of petroleum or similar hydrocarbons into acids, the author recommends heating them in a current of air or oxygen with substances having an alkaline reaction. Chloride of lime may also be employed, the oxidation being effected at 130—200°, after which the lime is removed by hydrochloric acid, and the remaining oily compound (after separation of the acids) is treated with about 50 per cent. of caustic soda at 200—300°. In some cases, nitric acid may be used as the oxidising agent. The fatty acids produced are separated by distillation under reduced pressure. The most volatile acids give with methyl, ethyl, butyl, or amyl alcohol, useful aromatic ethereal salts suitable for perfumes; the acids of higher constitution are nearly related to oleic acids, and their sulphonic acids may be used in Turkey-red dyeing. D. B.

Experiments with the Small Danish Separator. By M. Schmöger (*Bied. Centr.*, 1885, 635—637).—The narrowest ratio of cream to skim milk obtained by this centrifugal machine was 1 : 5. New milk can be more thoroughly creamed than milk which has stood. E. W. P.

Inorganic Constituents of Cheese. By W. Eugling and L. Mähr (*Bied. Centr.*, 1885, 637—639).—In normal curd, there is present 8·25—8·5 per cent. of earthy phosphates, the lime sometimes being to a certain extent replaced by magnesia. As a rule, in the caseïn free from fat, 4—4·4 per cent. of phosphoric acid is present. Best cheese contains 0·12—0·2 per cent. magnesia, if more than that is present, then the cheese is short, if less it will be doughy. All food for cows whose milk is converted into cheese must contain a plentiful supply of calcium phosphate, so that if such food as sugar manufactory waste is given, then 25—50 grams of precipitated phosphate must be added daily. E. W. P.

Manufacture of Magenta. By P. Schoop (*Dingl. polyt. J.*, **258**, 276—284).—The author discusses in detail the manufacture of magenta by the arsenic acid process. In the original paper, a lengthy table is given illustrating the extraction of the magenta melt by fractional precipitation. D. B.

Preparation of New Colouring Matters. (*Dingl. polyt. J.*, **258**, 87—91.)—For the preparation of benzylmethylaniline, Stebbens recommends heating 1 part of methylaniline with 2 parts benzyl chloride for four hours. Benzylmethylaniline boils at about 360°, and yields a nitro-compound which is reduced by zinc-dust to a paramido-compound. To obtain a dye resembling malachite-green, 2 parts of benzylmethylaniline are heated on a water-bath with 1 part of benzaldehyde and 1 part of zinc chloride until all odour of benzaldehyde has disappeared. The mixture is then rendered alkaline, and the oily leuco-base extracted with ether. On heating the latter with 0·5 part of chloranil, a green dye is obtained.

To prepare blue or violet colouring matters, the *Société Anonyme des*

Matières Colorantes de St. Denis employ the product of the action of dimethylaniline on acetone; dimethylaniline (2 mols.) and acetone, or its homologues (1 mol.), being heated under pressure at 150° with zinc chloride. After purification with benzene, the product yields colouring matters when subjected to oxidation.

According to the *Farbenfabriken, vormals F. Bayer und Co.*, perchloromethyl mercaptan, CCl_4S, obtained by the action of chlorine on carbon bisulphide, yields blue or violet dyes belonging to the rosaniline-group when heated gently with tertiary aromatic amines such as dimethylaniline, methyldiphenylamine, methylethylaniline, diethylaniline, diamylaniline, dibenzylaniline, methylbenzylaniline, dimethylorthotoluidine, diethylorthotoluidine, dimethyl-α-naphthylamine, and diethyl-α-naphthylamine. The same *Farbenfabriken* have patented a process for preparing yellow azo-dyes from benzidine and its homologues by suspending 10 kilos. of benzidine sulphate or hydrochloride in 150 litres of water, adding 20 kilos. of hydrochloric acid of 21° B., and diazotising with 2·5 kilos. of sodium nitrite. The solution of tetrazodiphenyl thus obtained is then treated with amidobenzenesulphonic acid (prepared by adding 9 kilos. of hydrochloric acid of 21° B. to 11 kilos. of the sodium salt) and 40 kilos. of sodium acetate. After 12 hours' digestion a brick-red precipitate is formed which imparts to cotton a permanent yellow colour. Tetrazoditolyl or tetrazodixylyl may be substituted for tetrazodiphenyl and amidotoluene, or amidoxylenesulphonic acid for amidobenzenesulphonic acid. A similar yellow dye, having a green tone, is obtained by the action of diazobenzene-, diazotoluene-, or diazoxylene-monosulphonic acid on benzidine, diamidoditolyl, or diamidodixylyl-derivatives.

Gürke by replacing the phthalic anhydride employed in the preparation of galleïn by an equivalent amount of monochlorophthalic acid or other higher chlorinated phthalic acids or anhydrides, obtains chlorinated galleïns, which are converted into coeruleïns by heating with sulphuric acid in the usual manner.

For the preparation of quinoline-derivatives from the salts of aromatic amido-compounds and acetone, or its condensation products, the *Farbwerke, vormals Meister Lucius und Brüning*, recommend mixing aniline (3 mols.) with acetone (6 mols.) and nitrobenzene (1 mol.). The mixture is saturated with hydrogen chloride and heated in a retort through which hydrogen chloride is passing in a continuous stream. When the reaction is completed, the residue in the retort is diluted with water. The solution is freed from excess of nitrobenzene, unattacked acetone, and mesityl oxide formed during the reaction by heating with steam, it is then rendered alkaline, and the oily basic mixture is subjected to rectification. A base is obtained which boils at 257—258°, and has an odour similar to that of quinoline.

D. B.

New Method for Effecting Discharges on Fibre Dyed with Indigo. By C. A. Franc (*J. Soc. Chem. Ind.*, **4**, 24).—The chromic acid discharge impeding the entry of other colours, especially alizarin, in those places where the colour has been destroyed, owing to the retention of chromic acid by the fibre, the author proposes the

use of ammonium metavanadate. In the first series of experiments, a mixture consisting of 50 grams of dark British gum dissolved in 50 c.c. of hot water, 10 grams of sodium chlorate, 5 c.c. of acetic acid 6° T, 5 grams of tartaric acid and 0·05 gram of ammonium metavanadate was used, good results being obtained. It was subsequently found that the smallest quantity of vanadium necessary to effect the discharge was 0·01 gram of the ammonium salt. The goods are aged and steamed as in the case of aniline-black. By soaping the whites, the best results are obtained. D. B.

Titanic Acid as a Mordant. By J. Barnes (*J. Soc. Chem. Ind.*, **4**, 310).—The author found that precipitated titanic acid gave a reaction with alizarin very similar to that produced by alumina. Prepared pieces of cloth were therefore dyed with various colouring matters, and finally soaped. *Alizarin* gave a full red, although duller, and of a bluer shade than when alumina was used. *Alizarin-orange*—Full orange, considerably redder than with alumina. *Coeruleïn and alizarin-blue*—Dark green and full blue respectively, similar to the colours produced with alumina as mordant. *Preparation of Persian Berries*—Brownish-orange. *Tannic acid*—Buff, very similar to an iron-buff. *Logwood extract*—Dark grey, almost black. D. B.

Bleaching Wool with Hydrogen Peroxide. By C. H. Löbner (*Dingl. polyt. J.*, **258**, 96).—Before bleaching, the wool should be thoroughly washed. When commercial hydrogen peroxide is diluted with 10 parts of water, 30 to 40 minutes' immersion in the bleaching bath suffices. After the wool is taken out of the bath, the bleaching operation proceeds until the wool is dry, it is therefore preferable to retard the drying process as much as possible. To obtain pure whites, it is necessary to add a small quantity of indigo-carmine to the bath. D. B.

General and Physical Chemistry.

Peculiar Spectrum of Rare Earths of the Terbia Group. By L. DE BOISBAUDRAN (*Compt. rend.*, **102**, 153—155).—Some years ago the author described a peculiar spectrum which is observed when an induction spark is allowed to play upon the surface of a hydrochloric acid solution of the mixed earths commonly known as terbia. Further fractionations have given a product in which the only known metals giving spectra are holmium, terbium, and the compounds $Z\alpha$ and $Z\beta$ which produce fluorescence. This peculiar spectrum cannot be attributed to holmium and terbium, since its intensity does not vary as the proportions of either of these elements. It seems to be due to the fluorescent body $Z\alpha$, but the author provisionally attributes it to an unknown body, $Z\gamma$, which may or may not be identical with $Z\alpha$. The position and characteristics of the lines in this spectrum are given in the original paper. C. H. B.

Specific Refraction and Dispersion of the Alums. By J. H. GLADSTONE (*Phil. Mag.* [5], **20**, 162—168).—In this paper the results obtained by Soret and others of the refractive indices for the lines A and G, the specific refraction $\frac{\mu_A - 1}{d}$, specific dispersion $\frac{\mu_G - \mu_A}{d}$, and refractive equivalent $P\frac{\mu_A - 1}{d}$, for the various alums are collected. These figures confirm the conclusions: (1) that the specific refraction of a substance is the same whether in a solid form or in solution; (2) that the refraction equivalent of a compound is equal to the sum of the refraction equivalents of its components. The differences, however, of the equivalent produced by the replacement of one alkali metal or grouping by another is not constant for each series of alums. The observed dispersion equivalents of these salts are also fairly accordant with those calculated from their constituents, but the differences due to the substitution of one metal for another are very considerable. In the different series, the same order of magnitude of the dispersion equivalents is preserved, namely, thallium, methylamine, cæsium, ammonium, rubidium, potassium, and sodium, whilst in the iron group the order is iron, chromium, indium, gallium, and aluminium. The series is the same as that previously observed with the simple sulphates of these metals. V. H. V.

Cause of Irregularities in the Action of Galvanic Batteries. By H. V. HAYES and J. TROWBRIDGE (*Amer. J. Sci.*, **30**, 34—37).—By means of an apparatus for photographing the deflections of a galvanometer needle, the authors tested a number of batteries; all variations of current being accurately registered. Irregularities were found to be caused by two separate actions, a diminution in the current strength, caused by the pores of the parti-

tion becoming filled with the base, and, secondly, a diminution of the acid at the positive pole. Both these difficulties are overcome by making a partition of as large surface dimensions as possible, and by using very porous material. B. H. B.

Electrolytic Decomposition. By J. W. Clark (*Phil. Mag.* [5], **20**, 37—47).—Our knowledge of the atomic and molecular constitutions of substances is not sufficiently exact to permit of any definite conclusions regarding the conditions necessary for electrolytic and metallic conductivity with the exception of that of liquidity either by fusion or solution. But even here cases are known of substances, liquid under ordinary conditions, such as arsenic and stannic chlorides, which act neither as metallic conductors nor as electrolytes, and on the other hand certain solid compounds act as metallic conductors, whilst others of precisely similar constitution act as electrolytes. From a general examination of the researches of Faraday, Hittorf, Wiedemann, and others, it is concluded that certain solids possess, even at ordinary temperatures, a sufficient molecular mobility for electrolytic conduction, whilst in others it is induced by a rise of temperature insufficient for fusion, owing doubtless to an equalisation of strain, as exemplified by the annealing of glass. Secondly, substances of similar constitution may exhibit opposite forms of electric conduction, such as cuprous and silver sulphides and selenides. In this paper, the decomposition of mercuric iodide and chloride by electrolysis is examined. In the case of the former, when fused, iodine is liberated at the positive pole, being in part volatilised, in part dissolved within the fused salt; no metallic mercury appears to be liberated at the negative electrode, but mercuroso-mercuric iodide is formed, the reaction leading to its formation being as follows: (i) $2HgI_2 = Hg_2I_2 + I_2$; (ii) $2HgI_2 + Hg_2I_2 = Hg_4I_6$. There are no grounds for supposing that the electrolysis of the salt does not conform quantitatively to Faraday's law. It appears that the fused salt possesses great diffusibility, which would facilitate the mixture and decomposition of its products of electrolysis; the resistance of the fused salt is very great. By electrolysis, mercuric chloride is decomposed into chlorine and mercurous chloride, doubtless in accordance with Faraday's law; it is probable that some mercuroso-mercuric chloride is also formed, although this point is not fully examined. The great volatility of the salt, together with its high diffusive rate, facilitates the mixing and combination of the products of decomposition. The electric resistance of the fused substance is much higher than that of mercuric iodide. V. H. V.

Influence of the Composition and Constitution of Acids on their Electrical Conductivity. By W. Ostwald (*J. pr. Chem.* [2], **32**, 300—374).—The author in continuing his researches on "Electrical Conductivity" (Abstr., 1884, 3 and 323) has examined about 130 different inorganic and organic acids in different states of dilution (gram-molecule in n-litres). He conducts his experiments as described in former papers, and expresses his results in terms of *molecular conductivity*. G. H. M.

The Thermo-electric Position of Carbon. By J. BUCHANAN (*Phil. Mag.* [5], **20**, 117—125).—Many of the carbon filaments of incandescent lamps break near the point where the current passes from carbon to platinum. To see whether this arose from heat due to the "Peltier effect," the author determined its amount, and this he found to be only about one quarter per cent. of the total heat of the filament, and therefore too small to have any appreciable influence on the life of the lamp. The author determined the thermo-electric power of carbon, the value found being

$$e_c = -390 - 1{\cdot}87t \text{ C.G.S. units,}$$

and this shows that the place of carbon in the thermo-electric series is between zinc and silver. It was found that the thermo-electric power of carbon was changed by keeping that substance at a moderately high temperature. R. R.

Thermochemical Relations of the Acids and Alcohols of the Fatty Series. By F. STOHMANN (*J. pr. Chem.* [2], **32**, 420—424).—The author considers that since the conversion of the normal alcohols into acids of the fatty series takes place by the substitution of one oxygen-atom for two hydrogen-atoms in the group $CH_2{\cdot}OH$, there should be for the homologous series a distinct heat effect, which should be expressed by the difference of the heats of combustion of the alcohols and acids. The heats of combustion per gram-molecule of the alcohols are as follows:—

			Difference.
Methyl alcohol,	CH_4O ..	169830 cal.	
			154670
Ethyl ,,	C_2H_6O..	324500 ,,	
			155813
Propyl ,,	C_3H_8O..	480313 ,,	
			156393
Butyl ,,	$C_4H_{10}O$.	636706 ,,	
			156917
Amyl ,,	$C_5H_{12}O$.	793623 ,,	
			156159 × 3
Capryl ,,	$C_8H_{18}O$.	1262100 ,,	
			156148 × 8
Cetyl ,,	$C_{16}H_{34}O$.	2511282 ,,	
	Mean of differences		156097

These numbers give 156097 cal. as the mean increase in the heat of combustion of the alcohols for every increment of CH_2. This number is higher than the corresponding number for the fatty acids (154275 cal.) by 1822 cal.

Comparing the numbers for the alcohols with those for the corresponding acids, we get—

		Difference.
Cetyl alcohol, $C_{16}H_{34}O$	2511282 cal.	137138 cal.
Palmitic acid, $C_{16}H_{32}O_2$	2374144 ,,	
Capryl alcohol, $C_8H_{18}O$	1262100 ,,	122135 ,,
Caprylic acid, $C_8H_{16}O_2$	1139965 ,,	
Amyl alcohol, $C_5H_{12}O$.....	793623 ,,	116947 ,,
Valeric acid, $C_5H_{10}O_2$.....	676673 ,,	
Butyl alcohol, $C_4H_{10}O$	636706 ,,	114028 ,,
Butyric acid, $C_4H_8O_2$.....	522678 ,,	
		x 2

		Difference.
Propyl alcohol, C_3H_8O	480313 cal.	112368 cal.
Propionic acid, $C_3H_6O_2$.....	367945 „	
Ethyl alcohol, C_2H_6O	324500 „	111207 „
Acetic acid, $C_2H_4O_2$	213293 „	
Methyl alcohol, CH_4O	169830 „	110812 „
Formic acid, CH_2O_2	59018 „	

When the number of carbon-atoms in each of these substances is multiplied by the difference in value of the CH_2 group in the alcohol and acid series, and the product deducted from the above differences a constant difference is obtained.

$$137138 - 16 \times 1822 = 107986$$
$$122135 - 8 \times 1822 = 107559$$
$$116947 - 5 \times 1822 = 107837$$
$$114028 - 4 \times 1822 = 106740$$
$$112368 - 3 \times 1822 = 106902$$
$$111207 - 2 \times 1822 = 107563$$
$$110812 - 1 \times 1822 = 108990$$

Mean 107654

This mean difference enables the author to calculate the heat of combustion of any fatty acid, when that of the corresponding alcohol is known, and also the heat of combustion of any alcohol when that of the acid is known.

For calculating the alcohols from the acids, the formula is—heat of combustion of acid + 107654 + ($n \times 1822$) = heat of combustion of alcohol, n being the number of CH_2 groups in the acid. Using this formula the following are the calculated heats of combustion of the alcohols :—

Methyl alcohol.....	168494 cal.	
Ethyl „	324591 „	156097
Propyl „	481056 „	156465
Butyl „	637611 „	156555
Amyl „	793431 „	155820
Capryl „	1262186 „	156252 × 3
Cetyl „ (liquid)	2510941 „	156094 × 8
	Mean difference....	156163

which closely agree with the found numbers. G. H. M.

Heats of Combustion of the Fatty Acids. By F. Stohmann and P. Rodatz (*J. pr. Chem.* [2], **32**, 407—420).—This is a continuation of previous work (Abstr., 1885, 857, 1176). The authors have determined the heat of combustion of the silver salts (Col. I), and from these calculated the numbers for the acids (Col. II).

Heat of Combustion per gram-molecule.

	Silver salt.	Free acid.	
Acetic acid.....	191549 cal.	213293 cal.	154652
Propionic acid ..	345529 „	367945 „	154733
Butyric „ ..	499590 „	522678 „	153998
Valeric „ ..	652916 „	676676 „	154570
Caproic „ ..	806814 „	831246 „	154359 × 2
Caprylic „ ..	1114189 „	1139965 „	154748 × 2
Capric „ ..	1422342 „	1449462 „	153859 × 2
Lauric „ ..	1728717 „	1759181 „	153708 × 2
Myristic „ ..	2034790 „	2064598 „	
Benzoic „ ..	746770 „	—	—
Salicylic „ ..	694330 „	—	—
		Mean of difference....	154275

As a control to these numbers, direct determinations were made with the following acids:—

	Heat of combustion per gram-molecule.	
	Silver salt.	Free acid.
Caproic acid (liquid)....	831246	830212 = 100 : 99·9
Capric „ „	1449462	1455636 = 100 : 100·4
Lauric „ „	1757181	1756338 = 100 : 99·9
Myristic acid „	2064598	2064649 = 100 : 100·0

Using 154275 cal. as the mean increase for each increment of CH_2, the following numbers were obtained:—

		Calculated.	Found.
Lauric acid (solid),	$C_{12}H_{24}O_2$ ..	—	1747600
Myristic acid (solid),	$C_{14}H_{28}O_2$ ..	2056150	2053824 = 100 : 99·9
Palmitic „ „	$C_{16}H_{32}O_2$ ..	2364700	2361856 = 100 : 99·9
Stearic „ „	$C_{18}H_{36}O_2$ ..	2673250	2677834 = 100 : 100·2

From these experiments, and the fact that Thomsen found 60193 cal. for the heat of combustion of formic acid, the authors conclude that the heat of combustion of the fatty acids increases by 154275 cal. for every increment of CH_2. G. H. M.

Thermochemistry of Glyoxylic Acid. By DE FORCRAND (*Compt. rend.*, **101**, 1495—1498).—Alcohol was slowly oxidised by ordinary nitric acid, and the product was neutralised with calcium carbonate as in Debus' process, but the calcium glyoxylate was found to be contained mainly in the precipitate insoluble in cold water. It was extracted from this precipitate by repeated treatment with boiling water, and purified by crystallisation. The calcium glyoxylate was exactly decomposed by oxalic acid, and the solution concentrated on the water-bath and in a vacuum until the glyoxylic acid crys-

tallised. The crystals have the composition $C_2H_4O_4$, are very deliquescent and very soluble in water. Heat of solution at 10—12° = −2·5 cal.; heat of neutralisation with NaHO + 13·23 cal.; with CaH_2O_2, + 14·02 cal.; with NH_3 + 12·15 cal. These values agree closely with those obtained in the case of acetic, glycollic, and oxalic acids.

Sodium glyoxylate forms crystals of the composition $C_2H_3NaO_4$, which do not lose water at 110—120°. Heat of solution at 10° = −4·80 cal.; heat of formation from solid acid and solid hydroxide, +26·76 cal. Calcium glyoxylate crystallises in brilliant silky needles, which lose water at 110—120°, and then have the composition $(C_2H_3O_4)_2Ca$. Heat of solution at 10° = −2·24 cal.; heat of formation from solid acid and solid hydroxide = +31·14 cal. The heats of formation of the corresponding glycollates are +24·64 cal. and +26·98 cal. respectively.

The addition of excess of soda to neutral solutions of sodium glyoxylate causes a development of heat.

$C_2H_3NaO_4$ + NaHO develops + 2·01 cal.
$(C_2H_3NaO_4$ + NaHO) + NaHO develops + 0·64 cal.

The number 2·01 cal. is much lower than that which would correspond with a second acid function, but is considerably higher than that corresponding with the alcoholic function of glycollic acid. This development of heat is due to the aldehydic function of the gloxylic acid, and the fact that it is small compared with the heat developed by the action of soda on aldehyde is due to the dissociation of the aldehydate by the water present. The addition of a second equivalent of alkali diminishes this dissociation. C. H. B.

Method for Determining Vapour-densities at a Known Temperature. By L. F. Nilson and O. Pettersson (*J. pr. Chem.* [2], **33**, 1—17).—A modified form of V. Meyer's apparatus is described, by means of which the vapour-density and the exact temperature at which it is observed can be determined at the same time; the vapour-density apparatus serves as an air-thermometer, the large capacity of the tube leading from the reservoir being compensated for and the error eliminated by an arrangement already described by Pettersson (*ibid.* [2], **25**, 102). The results yielded by this apparatus are very exact, and the authors recommend the method for determinations at low as well as at high temperatures. Beryllium chloride was prepared by passing dry hydrogen chloride (prepared from sublimed ammonium chloride and sulphuric acid) over the metal heated in a platinum tube. The chloride sublimes through platinum gauze into the cool part of the tube. That part of the tube containing the chloride is subsequently cut off, weighed in a glass tube, and dropped into the vapour-density apparatus; the platinum is afterwards weighed alone. To control the experiment, the amount of hydrogen formed in preparing the chloride is measured.

The following vapour-densities of beryllium chloride (air = 1) were obtained at the given temperatures:—

t.	*d.*	*t.*	*d.*
490°	6·7	745°	2·753
520	4·174	812	2·793
589	3·067	1080	2·684
597	3·031	1115	2·779
604	3·090	1184	2·824
686	2·853	1502	2·791
720	2·926	—	—

In the first two experiments (at 490° and 520°), the substance was only slowly volatilised, whilst at the higher temperatures the substance behaved normally. N. H. M.

Vapour-densities of some Ethereal Salts. By N. Menschutkin and D. Konovaloff (*Ber.*, **18**, 3328—3330).—The authors refer to a previous communication (Abstr., 1884, 1119) in which the results of vapour-density determinations of amyl chloride, repeated without emptying the apparatus, were given, and add two more series of observations since made representing the progress of the decomposition of amyl chloride at 182°. These results show that the abnormal density of amyl chloride, as found by the authors, is not due to the glass of the apparatus being attacked as was contended by Alexéeff (this vol., p. 116); were this the case, the observations made on repeating the experiment would be the same as the last observation of the first series of experiments, and the reunion of the products of decomposition could not be complete on cooling the apparatus.

N. H. M.

Application of the Numerical Laws of Chemical Equilibrium to the Dissociation of Chlorine Hydrate. By H. le Chatelier (*Compt. rend.*, **101**, 1484—1487).—The author's formula for the conditions of chemical equilibrium of gaseous systems (this vol., p. 196) indicates that the tension of dissociation of chlorine hydrate and analogous compounds is not constant at a given temperature, but varies with the conditions of the experiment. Previous experiments with chlorine hydrate have led to the conclusion that its tension of dissociation is constant at a constant temperature, because the observations have been made in the presence of pure water, the tension of which is constant at a given temperature. Under these conditions, the tension of the liberated chlorine is also constant, as the formula indicates, and hence the tension of dissociation, which is the sum of the tensions of these two compounds, is likewise constant. If, however, the tension of the water vapour at constant temperature is caused to vary by dissolving in it some foreign matter, such as sodium chloride or hydrochloric acid, the tension of dissociation of the chlorine hydrate is rapidly modified.

Heat of solution of chlorine hydrate $Cl_2,8H_2O = -14$ cal.; heat of formation $Cl_2 + 8H_2O$ liquid $= +17$ cal.; $Cl_2 + 8H_2O$ gas $= +102$ cal. C. H. B.

Theory of Solution. By W. W. J. Nicol (*Proc. Roy. Soc. Edin.*, **119**, 27—29).—An account of the experimental evidence in support of the theory of solution enunciated in a paper "On the Nature of Solution" (Abstr., 1883, 253).

Supersaturation of Salt Solutions. By W. W. J. Nicol (*Phil. Mag.* [5], **19**, 453—461; and **20**, 295—300).—Supersaturation is generally defined as the existence in solution at any given temperature of a greater quantity of salt than can be dissolved at that temperature by the addition of water to salt. But such a phenomenon includes the two cases of the presence and absence of undissolved salt respectively. The former case is dependent on the time required for the establishment of equilibrium between the water and salt molecules. Kremer's experiments, as also those of the author, have shown that too little attention has been paid to this point in determinations of the solubility of salts.

The second case is the true phenomenon of supersaturation, and occurs only with salts which form hydrates. In these papers, this point is discussed with a view of demonstrating that the so-called supersaturated solution is merely a solution of the anhydrous salt below or at the immediate point of its saturation. Experiments made with sodium sulphate and thiosulphate showed that there was no point of discontinuity in the densities and specific volumes of solutions of these substances from the point of saturation under ordinary conditions up to that of the fused crystalline salt. Such are in fact solutions of the anhydrous salts as yet unsaturated. Were this view correct, these solutions saturated with crystals of the hydrate should dissolve the same salt when in a dehydrated condition. This was confirmed by experiment, thus offering another proof of the author's view that a salt exists in solution not in the hydrated, but in the anhydrous state. Otherwise, there does not appear to be any explanation of the fact that the water of crystallisation possesses the same volume as that of solution. Then the kind of matter in solution is not the same as the crystalline hydrate, and it is to this that the phenomenon of supersaturation is due.

Now it is a commonly received opinion that the solution of an anhydrous salt in pure water takes place in two successive stages: (i) the hydration of the solid; (ii) the solution of that hydrate. In a comparative experiment, the same quantity of dehydrated sodium sulphate was sealed up in two glass bulbs and put into the same quantity of distilled water in two similar vessels, of which one was maintained constantly at 20°; the other, heated for some time to 100°, and then cooled to 20°. Then on breaking the bulbs the salt contained in the latter dissolved readily; that in the former very slowly. In this case the solid hydrate is formed, whilst in the other, solution takes place immediately without preliminary hydration.

The cause of so-called saturated solutions crystallising in contact with air and of their non-formation by the direct addition of water to the anhydrous salt, is the presence of fragments of the hydrated salt either within the containing vessel or the mass of dehydrated salt.

In conclusion, the great rise of temperature attending the solution of the salt, equal to if not greater than that in the solution of the dehydrated salt under ordinary conditions, as correlated with the change of volume, is briefly discussed. V. H. V.

Rate of Chemical Change as a Function of Temperature. By J. J. Hood (*Phil. Mag.* [5], **20**, 323—328).—Harcourt and Esson, from their observations on the rate of chemical change as a function of temperature, concluded that if α be the rate of change in any system at 0° C., the rate α' at another higher temperature $t°$ is $\alpha' = \alpha k^t°$, in which k is a constant, varying according to the nature of system. In the particular case examined, that of hydrogen dioxide and hydrogen iodide the value for k was 1·07 (this Journal, 1867, 492). In the paper, this point is further examined in the case of the system, ferrous sulphate, potassium chlorate, and sulphuric acid, within the limits of temperature 10—32°. Below this limit the progress of change was so slow that incidental errors occurred, whilst above, it was too rapid for accurate observation. The equation deduced from the experiments is of the same exponential form as that above, namely, taking α, the rate at 10°, as unity, the rate at another higher temperature $t°$, is expressed by $\alpha' = k^{t-10}$, in which the value for $k = 1·093$ for this particular system. V. H. V.

Apparatus for Chemical Laboratories. By J. Walter (*J. pr. Chem.* [2], **32**, 425).—These consist of an arrangement by means of which a current of warm air or steam can be passed round a dish or beaker placed in the exsiccator, there being also an arrangement by which the substance in the exsiccator can be treated with a solvent, or any volatile liquid distilled off: a modification of the ordinary separating funnel, and also one for the decomposition of substances with acids. G. H. M.

Thermo-regulator. By U. Kreusler (*Chem. Centr.*, 1885, 739—740, from *Chem. Zeit.*).—A modification of the mercurial thermo-regulator, a governor being also employed to prevent variations due to sudden changes of pressure in the gas.

Inorganic Chemistry.

Decomposition of Chlorine-water in Sunlight. By A. Popper (*Annalen*, **231**, 137—143).—The author confirms his previous statement (Abstr., 1885, 631) that an aqueous solution of chlorine decom-

poses on exposure to sunlight, yielding chloric and hydrochloric acids and oxygen. No perchloric acid is formed. The decomposition may be represented as follows: $5Cl_2 + 5H_2O = HClO_3 + 9HCl + O_2$.

W. C. W.

Remarks on Popper's Experiments on the Decomposition of Chlorine-water by Sunlight. By L. Pebal (*Annalen*, **231**, 144—152).—When chlorine-water is decomposed by exposure to sunlight, the evolution of oxygen ceases as soon as the free chlorine disappears. This indicates that the oxygen is evolved during the formation of the chloric acid, and is not due to its decomposition.

Hypobromous and bromic acids are much less stable than the corresponding chlorine compounds. When bromine-water is exposed to bright sunshine, only a very small quantity of these acids is produced.

W. C. W.

Production of Ozone by the Slow Oxidation of Phosphorus. By R. Engel (*Bull. Soc. Chim.*, **44**, 426—427).—Phosphorus exposed to the air in a glass vessel surrounded by melting ice does not form ozone, nor does it show any luminosity. If, however, the pressure of the air is reduced, ozone is formed, and the phosphorus becomes luminous.

A. P.

Purification of Sulphuric Acid. By Kupferschläger (*Bull. Soc. Chim.*, **44**, 353—355).—The acid is diluted with its own weight of water, treated with excess of washed sulphurous anhydride, and subsequently the acid is saturated with hydrogen sulphide, the sulphides of lead, arsenic, and selenium are allowed to settle, and the clear acid poured off and distilled.

A. P.

The Action of Sulphurous Acid on Selenious Acid. By H. Schulze (*J. pr. Chem.* [2], **32**, 390—407).—Rose (*Ann. Phys. Chem.*, **113**, 472) stated that pure solutions of sulphurous and selenious acids are without action on each other, and that it is necessary to add hydrochloric acid in order to obtain a precipitate of selenium. The author however, finds that when the pure solutions are mixed in certain proportions (4 parts SeO_2 to 4·7 parts SO_2) selenium is at once precipitated, but if either a larger quantity of SeO_2 or of SO_2 is used, only a coloration is produced. This reaction corresponds with the equation $2SO_2 + SeO_2 + 2H_2O = Se + 2H_2SO_4$. A considerable rise of temperature takes place when the solutions are mixed, and using Thomsen's numbers the author finds that 71100 cal. are liberated in the above equation. In mixtures of the pure solutions *not* in the above proportions, the author has found soluble colloïdal selenium. This may be obtained as a dark-red powder, completely soluble in water to a red solution; the solution is decomposed in sunlight, and on dialysis gives the pure colloïdal form of selenium. When an excess of sulphurous acid is used above that required for the above equation ($2SO_2 : SeO_2$), an acid is apparently formed in the liquid according to the equation $3SO_2 + SeO_2 + 2H_2O = H_2S_2SeO_6 + H_2SO_4$, and when an excess of selenious acid is used, the formation of an acid apparently takes place according to the equation $2SO_2 + 2SeO_2 +$

$2H_2O = H_2SSe_2O_6 + H_2SO_4$. Neither these acids nor their salts could be obtained in a state of purity. G. H. M.

Phosphorus Pentafluoride. By H. Moissan (*Compt. rend.*, **101**, 1490—1492).—When a current of phosphorus trifluoride is passed into bromine cooled to $-15°$, phosphoric fluobromide is formed, and this compound decomposes spontaneously into phosphorus pentabromide, a solid substance, and phosphorus pentafluoride, $5PF_3Br_2 = 3PF_5 + 2PBr_5$. Phosphorus pentafluoride is a colourless gas, which fumes strongly in the air, has a pungent odour, and is completely soluble in water; density 4·49. It liquefies under a pressure of 46 atmos. at 15°, and the liquid does not attack glass. If the pressure is partially released the gas solidifies, but rapidly returns to the liquid condition. Notwithstanding the care taken in drying the gas, a certain quantity always remains unliquefied, but if the pressure is raised from 46 atmos. to 125 atmos. the meniscus disappears. The whole of the space above the mercury has the same index of refraction. This is the critical point, and hence it is possible by means of phosphorus pentafluoride to exhibit the liquefaction, solidification, and critical point of a gas at the ordinary temperature (comp. Thorpe, this Journ., 1877, i, 46; also *Proc. Roy. Soc.*, **25**, 122). C. H. B.

Hydrates of Hypophosphoric Acid. By A. Joly (*Compt. rend.*, **102**, 110—112).—In a dry vacuum, the crystals of the hydrate $P_2O_4,4H_2O$ (this vol., p. 201) lose water without efflorescing, partially liquefy, and are gradually converted into small crystals of the normal hydrate, $P_2O_4,2H_2O$. This hydrate is very hygroscopic; it melts at about 55°, forming a colourless, transparent liquid, which completely solidifies in contact with a fragment of the original solid. If, however, the temperature is allowed to rise to about 70°, the hydrated hypophosphoric acid suddenly decomposes with considerable development of heat into a mixture of phosphorous and metaphosphoric acids.

The hydrate $P_2O_4,4H_2O$ melts at 62—62·5°, but the superfused liquid gradually deposits snow-like crystals, which probably consist of the normal hydrate, and the supernatant liquid no longer solidifies completely in contact with a crystal of the original hydrate. If this hydrate is exposed to dry air under ordinary pressure, it effloresces slightly, and the effloresced crystals begin to melt at about 53°, gradually splitting up into water and the normal hydrate. The crystals of both hydrates are perfectly stable out of contact with water, but in contact with water they are rapidly converted into phosphoric and phosphorous acids. This change takes place if the original crystals of $P_2O_4,4H_2O$ are allowed to remain in contact with the mother-liquor.

In preparing hypophosphoric acid, elevation of temperature and excess of sulphuric acid should be avoided. C. H. B.

Polymerization of the Metallic Oxides. By L. Henry (*Phil. Mag.* [5], **20**, 81—117).—This paper discusses and advances proofs of the following propositions:—The known oxides, and notably the metallic oxides, are polymerides, $n(RO_x)$, of the true normal oxides, RO_x, corresponding with the chloride RCl_2x. Among the

considerations relied on, is the comparison of the physical properties of the oxides and those of the corresponding chlorides. The smaller atomic weight and higher volatility of oxygen as compared with chlorine might be expected, *a priori*, to so influence the compounds that the oxides would be more fusible and more volatile than the corresponding chlorides. This is actually the case in a number of instances, for example, SO_2 and $SOCl_2$; SO_3 and SO_2Cl_2; CO_2, $COCl_2$, and CCl_4. The like relationship holds between the oxides and the chlorides of the bivalent radicles, C_nH_{2n}. But if we compare metallic chlorides with metallic oxides, we find that whilst the chlorides are fusible and volatile compounds, the oxides are, on the contrary, distinguished by their fixity and infusibility. The formulæ of the chlorides have usually been deduced from their vapour-densities, whilst the formulæ of the oxides depend solely on analytical determinations, and represent merely the relative weights of the constituents. The similarity of constitution between the oxides and chlorides, as represented by the usual formulæ, is therefore a pure assumption.

A marked increase of sp. gr. is observed in the case of known polymerides, *e.g.* :—

	Mol. weight.	Sp. gr.
C_5H_{10}, amylene	70	0·663
$C_{10}H_{20}$, diamylene	140	0·777
$C_{15}H_{30}$, triamylene	210	0·814

It is also observed that the sp. gr. of oxides of the C_nH_{2n} radicles are notably less than those of the corresponding chlorides, and the difference is in some degree similar to that between the molecular weights of these compounds. But the sp. gr. of the oxides and chlorides exhibit very marked inverse differences; for example:—

	Mol. weight.	Sp. gr.
$CaCl_2$.....	111	2·16
CaO	56	3·20
$ZnCl_2$.....	136	2·75
ZnO	81	5·73
$CdCl_2$.....	183	3·62
CdO	128	6·95

From this again, it seems that the metallic oxides cannot be molecularly comparable with the chlorides; that the true oxides which would be so comparable are unknown, and that we possess only their polymerides. It is as yet impossible to assign the value of the coefficient n of polymerization, or the real molecular formula to any one of these oxides. We may, however, infer from known facts that this coefficient must be always very high, and different for the various oxides.

In the valencies of chlorine and of oxygen, we find the mecha-

nism of this molecular condensation in the oxides, and its absence in the chlorides. Oxygen, by its two affinities, can unite radicles belonging to two different molecules, and this may be presumed to occur in the dehydration of metallic hydroxides; whilst in cases of chlorides, chlorine being monovalent, cannot directly unite with two other atoms. The act of polymerization may be observed in certain anhydrous and pulverulent metallic oxides, obtained by dehydration of their hydroxides at as low a temperature as possible. These, when exposed to a temperature approaching redness, suddenly enter into vivid incandescence, and become denser, harder, and deeper coloured than before. They offer a greater resistance to reagents, some not being attacked by acids or alkalis. Fe_2O_3, Cr_2O_3, ZrO_2, are examples.

The author proposes to classify oxides into *normal oxides*, such as SO_2, CO_2, NO, N_2O_3, &c., and *polymerized oxides*. The latter class he subdivides according to their behaviour with heat in relation to depolymerization. R. R.

Peroxides of Zinc, Cadmium, Magnesium, and Aluminium. By J. Gibson and R. M. Morrison (*Proc. Roy. Soc. Edin.*, **119**, 146—152, and 152—194).—Whilst attempting to remove cerium from a solution of lanthanum and didymium by means of magnesia, and subsequent addition of hydrogen peroxide, a precipitate was formed, which gave rise to the suspicion that a peroxide of magnesium had been produced. As a result of these observations, peroxides of various metals have been formed in the following manner:—100 c.c. of a solution of zinc sulphate, containing 5 grams per c.c., was mixed with 450 c.c. of a solution of ammonia (0·037 NH_3 per c.c.); after filtration 100 c.c. was mixed with 350 c.c. of dilute solution of hydrogen peroxide. The precipitate produced is yellowish-white, is soluble in cold dilute acids, and shows the properties of a peroxide, but the percentage of oxygen is variable, the variation depending on modifications in the process of preparation. The cadmium peroxide prepared in a similar manner is buff-coloured, and this, as well as the magnesium peroxide, contains varying proportions of oxygen. The aluminium compound was obtained by dissolving 100 grams ammonium alum in a sufficiency of water, and then adding alkali until the precipitate formed was nearly dissolved; this solution, on the addition of hydrogen peroxide, yields the peroxide; the precipitate, when dried at 100°, contained 1·04 per cent. O, dried in a vacuum 1·6 per cent. beyond that corresponding to the ordinary oxide, consequently this compound resembles the others described.

The authors claim precedence over Haas, Clève, and Boisbaudran, as regards the discovery of the compounds mentioned in the preceding article, for although the paper is only now published, it was read before the Society in 1880. Further, they controvert some of the statements of Haas and Clève. E. W. P.

Solubility of Cupric Sulphate in Presence of Ammonium Sulphate. By R. Engel (*Compt. rend.*, **102**, 113—115).—Two flasks, kept at a temperature of 0° by being surrounded with melting

ice, were partially filled with a saturated solution of cupric ammonium sulphate, a quantity of the double salt being suspended in a basket in the upper part of the liquid, which was agitated by a slow current of air. After 24 hours, a quantity of a saturated solution of cupric sulphate was added to one flask, and a quantity of a saturated solution of ammonium sulphate to the other. Portions were taken from each flask after 24 and 48 hours, and were analysed. A further quantity of ammonium sulphate or cupric sulphate was then added, and the experiment continued in the same way.

The effect of an increase in the quantity of ammonium sulphate is to precipitate cupric sulphate in the form of the double salt. If some of the double sulphate is left in contact with a saturated solution of ammonium sulphate at 0°, the latter remains colourless, or at most acquires a faint bluish tinge. The sum of the molecules of the two salts is not at a minimum when the quantities of each salt in solution are equal, but only when ammonium sulphate is present in much higher proportion.

If the quantity of ammonium sulphate increases in geometric progression, the quantity of cupric sulphate diminishes in geometric progression, the curve being represented by an equation of the form $m \log y = \log k - \log x$, in which y is the quantity of cupric sulphate, and x the quantity of ammonium sulphate, m and $\log k$ being constants, with the values 0·438 and 1·295460 respectively. The numbers calculated by means of this equation agree well with the results of experiment. C. H. B.

Formation of Ultramarine in the Wet Way. By F. Knapp (*J. pr. Chem.* [2], **32**, 375—390).—The author was led to make this investigation by observing that an ultramarine mixture of kaolin, soda, and sulphur, which had been heated and then allowed to stand exposed to a moist atmosphere, or moistened with liver of sulphur solution, gradually became blue.

In order to obtain a mixture which, after the preliminary heating, will give a good ultramarine in the wet way, it is necessary to pay attention to the following points:—The temperature to which the ultramarine mixture is heated; the nature and condition of the clay used; the length of time the mixture is heated; the behaviour of the silicate in the heated mixture when powdered; other changes in its chemical ingredients; the denseness or looseness of the mixture after heating.

The material used by the author was washed kaolin, with the following percentage composition:—Silica, 46·83; alumina, 40·25; water, 12·60; potash, 0·37; lime, trace; total, 100·05; and was expressed by the formula $2SiO_2 : 1·997AlO_3 : 1·79H_2O$.

The ultramarine mixture was made in the proportion—washed kaolin, 100 parts; anhydrous sodium carbonate, 100 parts; sulphur, 60 parts. The mixture was heated in small porcelain crucibles, holding 15—20 grams of the mixture; this was pressed in, and the top covered to a depth of 5—6 mm. with powdered charcoal, and the crucible then heated with the lid on. The mixture, after heating and separation from the charcoal, gives on digestion with solution of

liver of sulphur, the deep blue of ultramarine. Kaolin, digested alone with liver of sulphur solution, is unchanged. G. H. M.

Action of Reducing Agents on Vanadic Anhydride. By A. Ditte (*Compt. rend.*, **101**, 1487—1490).—Vanadic anhydride is not attacked by hydrogen at 100°, but reduction takes place slowly at 440°. Hypovanadic oxide is first formed, and this is reduced to vanadium trioxide, V_2O_3. The same change takes place more rapidly at a red heat.

If fused and powdered vanadic anhydride is heated at 440° in a current of hydrogen, the reaction is incomplete, because the hydrogen does not penetrate into the interior of the particles. The reaction is also incomplete if the vanadic anhydride contains hypovanadic oxide, and an intermediate oxide is formed which is not reduced by hydrogen at the given temperature. This oxide is obtained by heating ammonium vanadate in presence of air until the residue completely fuses, or by heating with an excess of vanadic anhydride the oxide formed by the decomposition of ammonium vanadate in a closed vessel. The product is extracted repeatedly with ammonia diluted with its own volume of water, and the intermediate oxide is obtained in brilliant needles or in small, brilliant, deep blue crystals of the composition V_2O_4,V_2O_5. This oxide is gradually dissolved by warm concentrated ammonia, but is only slightly soluble in strong nitric acid. It dissolves rapidly in hydrochloric acid with formation of a deep brown solution of the oxychlorides. It also dissolves in fused vanadic anhydride, to which it imparts a deep blue colour.

When ammonium vanadate is heated in a closed vessel, vanadium trioxide is obtained, mixed with a certain quantity of hypovanadic oxide. The formation of the latter is due to the entrance of air into the crucible.

Pure vanadium trioxide is readily obtained by heating ammonium vanadate in a closed vessel with an excess of sulphur or with an excess of ammonium oxalate.

If ammonium vanadate is heated in a closed vessel with an excess of powdered arsenic, crystals of a dark-blue intermediate oxide of the composition V_2O_3,V_2O_4 are obtained. It dissolves in cold nitric acid with formation of a blue solution. The same oxide is obtained in an amorphous condition when a mixture of ammonium vanadate and arsenic is heated in a long glass tube until all the arsenic is volatilised. When amorphous phosphorus is substituted for arsenic, hypovanadic oxide is obtained, and this combines with the phosphoric anhydride which is also formed, and produces hypovanadic phosphate.

When vanadic anhydride is heated in a current of sulphurous anhydride, reduction takes place slowly at a dull red heat, but at a higher temperature the anhydride melts, and when reduction is complete hypovanadic oxide is obtained in brilliant deep-blue needles. If ammonium vanadate is heated under the same conditions, the product is a dark-blue powder of the composition V_2O_3,V_2O_4.

By means of these methods of reduction, the following oxides can readily be prepared from vanadic anhydride in the dry way :—

V_2O_5,V_2O_4; V_2O_4; V_2O_4,V_2O_3; V_2O_3. C. H. B.

Antimony Sulphide and its Decomposition by Hydrochloric Acid. By BERTHELOT (*Compt. rend.*, **102**, 22—25, 84—86, 86—90). —The heat of formation of orange antimony sulphide was determined (1) by the action of an aqueous solution of hydrogen sulphide on a tartaric acid solution of antimony trichloride; (2) by the action of gaseous hydrogen sulphide on a solution of antimony trichloride in hydrochloric acid. The results obtained were practically identical: $Sb_2 + S_3 = Sb_2S_3$, orange, develops + 34·1 cal.

A solution of 100 grams of antimony chloride in a litre of hydrochloric acid, in which the ratio of acid to water is represented by the numbers $HCl : 3{\cdot}73H_2O$, gives no precipitate with hydrogen sulphide. On the other hand, dilute acid containing $HCl : 37H_2O$ dissolves only about 1 gram of antimony per litre. The heat of solution of antimony chloride in ordinary hydrochloric acid varies with the concentration of the acid, and diminishes as the proportion of salt already in the liquid increases.

The heat of formation of grey antimony sulphide was measured by dissolving it in sodium sulphide in the calorimeter, and also by decomposing a solution in sodium sulphide with hydrochloric acid. Both methods give the same result: $Sb_2 + S_3 = Sb_2S_3$, grey, develops + 34·0 cal. The heats of formation of the orange and of the grey variety are therefore identical and correspond with the development of 11·4 cal. for each atom of sulphur. Antimony therefore resembles copper, nickel, lead, and mercury in the energy with which it combines with sulphur, and antimony sulphide resembles other sulphides with low heats of formation in retaining to a certain extent the lustre and other physical properties of the metal.

The difference between the heats of formation of antimony trisulphide and the trioxide, 143·4 cal., explains the ease with which the former can be converted into the latter, the change being further facilitated by the tendency of the trioxide to take up an additional atom of oxygen.

The action between antimony trichloride and hydrogen sulphide on the one hand, and antimony trisulphide and hydrogen chloride on the other, is one of the most interesting of reversible chemical reactions. In the absence of water, the heat of formation of the first system exceeds that of the second by 30·6 cal.

$$\left.\begin{array}{lll} Sb_2 + 3Cl_2 = 2SbCl_3, \text{ cryst., develops} & + 182{\cdot}8 \text{ cal.} & \\ 3H_2 + S_3 = 3SH_2, \text{ gas,} \quad \text{,,} & + 13{\cdot}8 \text{ ,,} & \end{array}\right\} + 196{\cdot}6,$$

$$\left.\begin{array}{lll} Sb_2 + S_3 = Sb_2S_3, \quad \text{,,} & + 34{\cdot}0 \text{ ,,} & \\ 3H_2 + 3Cl_2 = 6HCl, \text{ gas,} \quad \text{,,} & + 132{\cdot}0 \text{ ,,} & \end{array}\right\} + 166{\cdot}0,$$

and it is well known that antimony sulphide is decomposed by gaseous hydrogen chloride. In presence of water, on the contrary, the heat of formation of the second system is 60·2 cal. higher than that of the first.

$$\left.\begin{array}{lll} Sb_2 + 3Cl_2 = 2SbCl_3, \text{ cryst., develops} & + 182{\cdot}8 \text{ cal.} & \\ 3H_2 + S_2 = 3SH_2, \text{ diss.,} \quad \text{,,} & + 27{\cdot}6 \text{ ,,} & \end{array}\right\} + 210{\cdot}4.$$

$$\left.\begin{array}{lll} Sb_2 + S_3 = Sb_2S_3 \quad \text{,,} & + 34{\cdot}0 \text{ ,,} & \\ 3H_2 + 3Cl_2 = 6HCl, \text{ diss.,} \quad \text{,,} & + 236{\cdot}6 \text{ ,,} & \end{array}\right\} + 270{\cdot}6.$$

The reversal of the reaction is mainly due to the combination of the hydrochloric acid with water. Between the two extremes there is a state of equilibrium corresponding with an intermediate proportion of water, this limit being chiefly determined by the proportion of water in presence of which anhydrous hydrogen chloride ceases to exist. It is already known that in aqueous hydrochloric acid the gas has no appreciable tension if the ratio of acid to water is below $HCl : 8—9H_2O$, but the tension becomes measurable at 12°, when the ratio is $HCl : 6{\cdot}5H_2O$. The tension is affected, although not to any great extent, by the presence of antimony trichloride. Direct experiment shows that hydrogen sulphide produces a slight turbidity in a solution of antimony chloride in which the ratio of acid to water is $HCl : 6{\cdot}4H_2O$, but a certain proportion of free hydrogen sulphide can exist in the liquid until the ratio of acid to water becomes $HCl : 7{\cdot}7H_2O$.

At a high temperature, the tension of the hydrogen chloride increases, and therefore solution of the sulphide will take place in presence of a larger proportion of water. Moreover, at 100° the sulphide is decomposed by water vapour with formation of an oxysulphide (Regnault).

The action of hydrochloric acid on antimony sulphide becomes practically *nil* when the ratio of water to acid reaches $8—9H_2O : HCl$, but this limit is modified by the production of a chlorosulphide,

$$2SbCl_3,5Sb_2S_3,$$

the heat of formation of which, 68 cal., is sufficient to reverse the reaction up to the point corresponding with the dissociation of this secondary compound or its decomposition by water. The tendency to the formation of antimony sulphide is augmented by an increase in the proportion of hydrogen sulphide, which tends to form hydrosulphides, but this effect is purely secondary and of no great magnitude. The formation of hydrosulphides increases in presence of a larger proportion of antimony sulphide, but diminishes in presence of unaltered antimony chloride. All these secondary reactions attain their maximum importance in the neighbourhood of the state of equilibrium, and under all other conditions exercise only a slight disturbing effect.

These results afford further confirmation of those principles of reciprocal action and conditions of equilibrium which have already been established. C. H. B.

Action of Antimony Sulphide on Potassium Sulphide. By A. Ditte (*Compt. rend.*, **102**, 168—170).—Hydrated antimony sulphide dissolves readily in a solution of potassium sulphide, and if the solution is evaporated in presence of excess of alkaline sulphide it deposits large, yellowish, transparent octahedra of the composition $2K_2S,Sb_2S_3$. These crystals are decomposed by water, which removes potassium sulphide, but they dissolve unchanged in a solution of the alkaline sulphide.

If a dilute solution of potassium sulphide is saturated with antimony sulphide and evaporated in a vacuum, it deposits small, red, transparent, prismatic crystals of the compound $K_2S,2Sb_2S_3 + 3H_2O$, which is decomposed when exposed to light.

When antimony sulphide, sulphur, and potassium carbonate are fused together in suitable proportions, the solution of the fused mass yields red crystals of the compound K_2S,Sb_2S_3, which is decomposed by water, potassium sulphide being removed, and an orange-red residue left.

If hydrated antimony sulphide is suspended in water, and a few drops of a solution of potassium sulphide are added, the antimony sulphide is more or less rapidly converted into a liver-coloured gelatinous mass.

If a solution of antimony sulphide in potassium sulphide is prepared in presence of excess of the former and filtered, it remains unaltered if preserved in a sealed tube; but if exposed to air it gradually deposits slender orange-red needles of the compound $K_2S,2Sb_2S_3$. If the solution is mixed with water, it is decomposed, and after some time sets to a reddish-yellow or deep red jelly.

When hydrated antimony sulphide is dissolved in a cold concentrated solution of potassium sulphide saturated with sulphur, a portion of the free sulphur is precipitated.

It is evident that the action of potassium sulphide on an antimony sulphide can convert the latter into a colloïdal variety, and then form double sulphides. C. H. B.

Compounds of Auric Chloride with Sulphur and Selenium Tetrachlorides. By L. Lindet (*Compt. rend.*, **101**, 1492—1495).—2—3 grams of spongy gold and 50 grams of sulphur chloride, S_2Cl_2, are heated at 130° until the gold is completely dissolved, and the flask is then closed and heated in an oil-bath at 160°. The slender yellow needles which separate are collected on glass wool and washed with dry carbon bisulphide. They have the composition $AuCl_3,SCl_4$, lose chlorine at the ordinary temperature, are hygroscopic, and are decomposed by water with formation of brown solutions, from which metallic gold gradually separates, whilst all the sulphur becomes converted into sulphuric acid.

In order to obtain the corresponding selenium compound, metallic gold is heated at 130° with a large excess of arsenic chloride containing an equivalent quantity of selenium tetrachloride in solution, and a current of dry chlorine is passed into the liquid until the gold dissolves. The solution when cooled deposits the compound $AuCl_3,SeCl_4$ in red, tabular crystals, which are dried in a vacuum at 65—70°.

Auric chloride dissolves in hot arsenic trichloride, silicon tetrachloride, antimony pentachloride, tin tetrachloride, and titanium tetrachloride; but when the solution cools, the auric chloride separates in large, dark-red, triclinic prisms, much flattened along the face *m*. In order to obtain crystallised auric chloride, the metal is attacked by chlorine in presence of one of these chlorides, which is kept at the boiling point. When the liquid cools, the auric chloride crystallises and is dried in a current of chlorine gas at a gentle heat.

Auric bromide dissolves in the same way in the corresponding bromides. C. H. B.

Three New Rhodium Compounds. By C. Vincent (*Bull. Soc. Chim.*, **44**, 513—515).—Compounds of rhodium sesquichloride with

the chlorides of mono-, di-, and tri-methylamine may be readily prepared by mixing a concentrated hot solution of rhodium chloride with an excess of the hydrochloride of the amine.

Monomethylamine chlororhodate, $Rh_2Cl_6(NH_2MeCl)_3$, forms long, slender, orthorhombic prisms of a fine garnet-red colour; it remains unaltered on heating at 140°.

Dimethylamine chlororhodate, $Rh_2Cl_6(NHMe_2Cl)_6 + 3H_2O$, forms large, dark, garnet-red, orthorhombic prisms; it effloresces in the air.

Trimethylamine chlororhodate, $Rh_2Cl_6(NMe_3Cl)_9 + 9H_2O$, forms long, garnet-red prisms; it is very soluble in water. On heating the above compounds, they fuse, become brown, intumesce, and are decomposed, leaving a residue of rhodium and carbon, which on ignition yields a spongy mass of slightly oxidised rhodium. The chlorine in these compounds cannot be estimated directly, owing to the formation of a silver chlororhodate; they are therefore fused with sodium carbonate and the chlorine titrated in the aqueous extract. A. P.

Mineralogical Chemistry.

Native Antimony from New Brunswick. By G. F. Kunz (*Amer. J. Sci.*, **30**, 275—277).—The Brunswick antimony mine is situated in Prince William parish, York Co., New Brunswick. In the early working of the mines, native antimony was only rarely observed. The mining was then all on the surface, but within the last two years it has been carried on to a considerable depth. At a depth of 100 to 150 feet native antimony is occasionally found in large pockets, some of which contain 1 ton of the pure mineral. It is associated with stibnite, valentinite, and kermesite.

In its most common form, the mineral is very compact and finely granular; it passes into a coarse granular variety resembling the native antimony of Borneo. The most remarkable form is that where it occurs in radiated masses of crystalline plates. Analysis gave the following results:—

	Gangue.	Fe.	As.	Sb.	Sp. gr.
I.....	0·84	0·11	0·86	[98·19]	6·606
II.....	5·04	0·34	0·47	[94·15]	6·693

I. Coarse-grained variety. II. Fine-grained variety.

The country rock is a black argillite, and the veins of quartz and calcite with stibnite, which traverse it, vary from 1 to 30 feet.

B. H. B.

Albertite from Strathpeffer, Ross-shire. By W. Morrison (*Min. Mag.*, **6**, 101—103; *Zeit. Kryst. Min.*, **11**, 178—179).—Albertite is found in thin veins in gneiss, micaceous sandstone, and conglomerate; sp. gr., 1·089. In 100 parts there are—

Volatile matter.	Fixed carbon.	Water.	Ash, sulphur.
62·00	37·00	0·60	trace

Analysis gave the following results:—

C.	H.	N.	O.	Ash.	Total.
79·75	8·12	1·63	10·30	0·20	100·00

The mineral becomes negatively electric by friction. The streak is black, not blackish-brown as in asphalt. B. H. B.

Crystallography of Bournonite. By H. A. Miers (*Min. Mag.*, **6**, 59—79; *Zeit. Kryst. Min.*, **11**, 175—177).—The observations of the author are the results of a study of the collection of bournonite in the British Museum. He gives a list of the 50 forms hitherto observed, to which he adds 29 new forms, about which there can be no doubt, and 21 doubtful forms of which isolated faces have been observed. B. H. B.

Rare Minerals from Hungary. By L. Sipöcz (*Ber.*, **19**, 95—105).—*Sylvanite* from Offenbánya: silvery white, prismatic and columnar crystals of sp. gr. 8·0733. Analysis gave—

Ag.	Au.	Cu.	Fe.	Te.	Total.
11·90	25·87	0·10	0·40	62·45	100·72

The probable formula is $5AgTe_2 + 6AuTe_2$.

Krennerite from Nagyág: pale steel-grey, strongly striated, cubical and prismatic crystals of sp. gr. 8·3533. Analysis gave—

Ag.	Au.	Cu.	Fe.	Te.	Sb.	Total.
5·87	34·77	0·34	0·59	58·60	0·65	100·82

The probable formula is $3AgTe_2 + 10AuTe_2 = Ag_3Au_{10}Te_{26}$.

Nagyágite from Nagyág: steel-blue, rectangular, tabular crystals of sp. gr. 7·4613. Analysis gave—

Pb.	Au.	Fe.	S.	Te.	Sb.	Total.
56·81	7·51	0·41	10·76	17·72	7·39	100·60

The probable formula is $Pb_{28}Au_4Te_{14}Sb_6S_{34}$, or $28PbS + 2Au_2Te + 3Sb_2Te_3 + 3TeS_2$, or $10Au(Sb)S_2 + 14PbTe + 14PbS$.

Wolframite from Felsöbánya: black, prismatic and tabular crystals of sp. gr. 7·4581. Analysis showed—

WO_3.	FeO.	MnO.	Total.
76·14	15·67	8·34	100·15

The probable formula is $MnFe''_2W_3O_{12}$, or $MnWO_4 + 2FeWO_4$.

Wehrlite from Pilsen: tin-white to grey, scaly masses of metallic lustre, which are very elastic and of perfect cleavage. The hardness of the edges is a little over 2, of the cleavage surface a little under 2. Two specimens were examined. One had a sp. gr. 8·368, and gave on analysis—

Ag.	Bi.	Te.	Total.
4·37	59·47	35·47	99·31

This agrees very closely with the formula $AgBi_7Te_7$. The second specimen gave on analysis—

Bi.	Te.	S.	Ag.	Total.
70·02	28·52	1·33	traces	99·87

Deducting the sulphur found as an impurity of bismuth sulphide, the probable formula is Bi_3Te_2. The two specimens of wehrlite are thus quite different in composition.

Nickel-ore from Orawitza: small, grey, crystalline fragments of sp. gr. 6·1977. Analysis gave—

						Residue insoluble in HNO_3 = 3·32.			
S.	As.	Bi.	Fe.	Ni.	Co.	Quartz.	Au.	Sb.	Total.
17·60	42·88	0·11	0·96	28·24	6·53	0·49	0·18	2·26	99·64

Disregarding the insoluble residue, this ore appears to be a gersdorfite (NiAsS), in which some of the nickel is replaced by cobalt. The nearest formula is 3CoAsS + 13NiAsS.

Grey nickel-ore from Dobsina: dark grey, crystalline masses showing hexahedral cleavage. The sp. gr. = 6·514, and analysis gave—

S.	As.	Fe.	Co.	Ni.	Total.
10·93	56·83	1·75	2·14	29·54	101·19

Deducting iron in the form of $FeAs_2$, the probable formula becomes $NiS_2 + 2NiAs_2$.

Red-nickel from Dobsina: rough masses of light coppery-red colour, and sp. gr. 7·5127. Analysis gave—

S.	Bi.	Fe.	Sb.	As.	Ni.	Total.
2·30	0·10	0·17	2·03	53·33	42·65	100·58

It thus appears to be NiAs with a little Sb_2S_5 present as impurity.

Semseyite from Felsöbánya: small, grey tabular crystals of sp. gr. 5·9518. Analyses gave—

S.	Sb.	Pb.	Fe.	Total.
19·42	26·90	53·16	0·10	99·58

This agrees closely with the formula $7PbS + 3Sb_2S_3$. Analyses are also given of four *zinc blendes*. Yellowish-brown translucent crystals of sp. gr. 4·0980 from Kapnik; brownish-red translucent crystals of sp. gr. 4·0635 from Nagyág; and yellow, translucent and highly lustrous crystals of sp. gr. 4·109 from Schemnitz, are all nearly pure ZnS, except that a little of the Zn is replaced by small and varying quantities of the isomorphous metals Cd, Mn, and Fe. A zinc blende from Rodna was obtained in the form of black, well-formed crystals of sp. gr. 4·0016. Its analysis gave—

Mn.	Fe.	Cd.	Zn.	S.	Total.
0·37	12·19	1·51	52·1	33·49	99·66

so that its composition leads to the probable formula $FeS + 4ZnS$ or $FeZn_4S_5$.

Bournonite from Nagyág: lustrous grey crystals of sp. gr. 5·7659. Analysis gave—

Pb.	Cu.	Fe.	Mn.	Zn.	Sb.	As.	S.	Total.
43·85	12·87	0·51	0·26	0·20	18·42	3·18	20·22	99·51

The simplest formula agreeing at all with these results would be $2PbS,Cu_2S,Sb_2(As)S_3$, but the more complex formula—

$$18Sb_2Pb_2Cu_2S_6 + 5As_2Pb_2Cu_2S_6,$$

is probably more correct. L. T. T.

Crystallised Tiemannite and Metacinnabarite. S. L. Penfield (*Amer. J. Sci.*, **29**, 449—454).—1. *Tiemannite.*—The author has examined crystals of a selenide of mercury from Marysvale, S. Utah, the same locality which afforded the sulphoselenide of mercury, onofrite, described by G. J. Brush (Abstr., 1881, 361). The crystals are black, with metallic lustre and black streak; H. 3; sp. gr. 8·188; fracture conchoidal, very brittle, and no apparent cleavage. Analysis gave the following results:—

Se.	S.	Hg.	Cd.	Insol.	Total.
29·19	0·37	69·84	0·34	0·06	99·80

The mineral may consequently be regarded as a simple selenide of mercury. The analysis agrees more closely with the theoretical requirements than any hitherto published, owing probably to the greater purity of the crystallised material. The crystals measure up to 3 mm. in diameter. They are isometric, tetrahedral, and in appearance resemble those of zinc blende.

2. *Metacinnabarite.*—In the specimens examined, from the Reddington mine, Lake Co., California, the mineral is intimately associated with cinnabar and marcasite. The crystals measure up to 4 mm. in diameter, and are apparently isometric tetrahedral. The habit of the crystal is octahedral with the alternate faces of the plus and minus tetrahedron varying in lustre. Sp. gr. 7·81.

Tiemannite and metacinnabarite are evidently isomorphous; whilst the intermediate chemical compounds to which the name of onofrite has been applied, and which are not known in crystals, take an intermediate position between the two in physical relations.

B. H. B.

Cerium, Yttrium, and Beryllium Oxides and Ammonium Chloride in Diluvial Clays. By J. R. Strohecker (*J. pr. Chem.* [2], **33**, 132—140).—The clay beds of Hainstadt, near Seeligenstadt, contain from 9·4 to 13·4 per cent. of cerium hydroxide. Beryllium oxide (5·38—6·43 per cent.) and small quantities of yttrium, lanthanum, and didymium oxides are also present. Ammonium chloride was found in the crystalline form in the clay. The methods employed for the separation of cerium are given. The oxides of cerium will become of technical importance as colours. N. H. M.

Hanksite. By W. E. Hidden (*Amer. J. Sci.*, **30**, 133—135).—Among the Californian minerals exhibited at the New Orleans Exhibition, was a small lot of apparently hexagonal crystals, to which had been given the name of thenardite. The correctness of this determination was doubted, as thenardite crystallises in the orthorhombic system. The crystals were found to be normally uniaxial with negative double refraction. An analysis gave the following results:—

SO_3.	CO_2.	Cl.	Na_2O.	Total.
45·89	5·42	2·36	46·34	100·01

This corresponds with the formula $4Na_2SO_4,Na_2CO_3,\frac{1}{2}NaCl$. Neglecting the sodium chloride as non-essential, the formula becomes $4Na_2SO_4,Na_2CO_3$.

The crystals are striated horizontally. They are usually terminated at both ends of the prism, and are very symmetrical. They average about 1 cm. in length and thickness, with 0P and ∞P as predominating planes. The crystals were found with salt, thenardite, and tincal, at the works of the San Bernadino Borax Company, California. The crystals are transparent to semi-opaque, with a white waxy colour. Sp. gr. 2·562. H. 3 to 3·5. The mineral is readily soluble in water, and effervesces with acids. For this new Californian mineral, the author proposes the name of Hanksite, after Prof. H. G. Hanks, of California. B. H. B.

A Large Crystal of Hanksite. By E. S. Dana and S. L. Penfield (*Amer. J. Sci.*, **30**, 136—137).—Two years ago, the authors examined a large crystal of an anhydrous sulphate related to thenardite. Feeling reluctant to give a new name to a mineral of which only one specimen was in hand, and that from an unknown locality, the authors postponed the publication of their results. The same mineral has now been rediscovered by W. E. Hidden (see preceding Abstr.).

The specimen examined consisted of a low hexagonal prism, penetrated by several other tabular crystals in varying positions. The basal edges were irregularly replaced by pyramidal planes. An analysis gave the following results:—

SO_3.	Na_2O.	CO_2.	K.	Cl.	Insol.	Ignition.	Total.
43·59	40·86	5·42	2·33	2·13	4·41	1·32	100·06

corresponding approximately with the formula $4Na_2SO_4,Na_2CO_3$.
B. H. B.

Gerhardite and Artificial Basic Copper Nitrates. By H. L. Wells and S. L. Penfield (*Amer. J. Sci.*, **30**, 50—57).—Gerhardite was identified as a new species by G. J. Brush, who found it among a lot of copper minerals from the United Verde Copper Mines, Jerome, Arizona. The specimen examined consisted of a small piece of pure cuprite, along a crack in which the new mineral and malachite occur. The hardness of the mineral is 2; sp. gr. 3·426; colour, dark green; streak, light green; transparent. The crystals are orthorhombic. There are two cleavages, one basal perfect, and a

second less perfect parallel to the macropinacoid. The axial ratio was found to be $a:b:c = 0{\cdot}92175:1:1{\cdot}1562$. Analyses gave the following results :—

	H_2O.	CuO.	N_2O_5.	Total.
I.....	11·49	66·26	[22·25]	100·00
II.....	11·26	66·38	22·76	100·40

The authors propose for this unique mineral, the only insoluble nitrate yet found in nature, the name *Gerhardite*, from the chemist who first determined the composition of the same compound made artificially.

Crystallised artificial basic cupric nitrate is made by heating a solution of the normal nitrate with metallic copper in a sealed tube at 150°, for a day or more. The crystals are of a dark-green colour, exactly like that of the mineral, with a very brilliant lustre. Sp. gr. 3·378. Their form is monoclinic, with a tabular habit; the axial ratio being $a:b:c = 0{\cdot}9190:1:1{\cdot}1402$; $\beta = 85°\ 27'$. The cleavage is the same as that of the natural nitrate. The crystals of the natural and of the artificial compound are very much alike, making an interesting case of dimorphism.

The results of two analyses of the artificial nitrate,

$$4CuO,N_2O_5 + 3H_2O,$$

were as follows :—

	H_2O.	CuO.	N_2O_5.	Total.
I	11·23	66·29	[22·48]	100·00
II	11·57	66·22	22·10	99·89

In conclusion, the results of previous investigators are summarised. The basic nitrate, $2(4CuO,N_2O_5) + 7H_2O$, described by Casselmann (*Zeit. anal. Chem.*, 1865, 24), is found on re-investigation to be identical with the basic nitrates made by other methods.

It is an interesting fact that the monoclinic mineral *tagilite*, has the formula $3CuO,P_2O_5 + 3H_2O$, exactly corresponding with that of the nitrate. B. H. B.

Meerschaum. By A. Damour (*Zeit. Kryst. Min.*, **11**, 206).—At Ablon (Seine-et-Oise) the author found a brown mineral resembling menilite, with sp. gr. 2·16 to 2·19. This gave on analysis—

SiO_2.	MgO.	Fe_2O_3.	H_2O.	Total.
83·08	6·73	1·00	9·20	100·01

By the action of the atmosphere, in a few months, a thick crust was formed on the mineral. This consisted of a white, pulverulent mass, giving on analysis the following results :—

SiO_2.	MgO.	FeO.	MnO.	H_2O.	Total.
61·20	18·70	0·80	0·30	18·60	99·60

corresponding with the formula $MgSi_2O_5 + 2H_2O$.

The meerschaum of Asia Minor occurs with a brown mineral of

sp. gr. 2·15. For the sake of comparison, this mineral was analysed, giving—

SiO_2.	MgO.	H_2O.	Total.
86·24	5·56	8·20	100·00

The porous crust of meerschaum gave—

SiO_2.	MgO.	H_2O.	Al_2O_3.	Total.
52·45	23·25	23·50	0·80	100·00

This gives the formula $Mg_2Si_3O_8 + 4H_2O$. B. H. B.

Cause of the apparently Perfect Cleavage in American Sphene. By G. H. Williams (*Amer. J. Sci.*, **29**, 486—490).—G. vom Rath (*Zeit. Kryst. Min.*, **5**, 495) has shown that the very perfect parting which exists in some varieties of pyroxene parallel to the basal pinacoid, is produced by the interposition of exceedingly thin twinning lamellæ. The author finds that the apparently perfect cleavage, so often observed in American sphene, is due to precisely the same cause; the cleavage being produced by a polysynthetic twinning parallel to the face η (−4P, Dana, −2P, Des Cloizeaux, $\frac{4}{5}P\bar{4}$ Rose). This explanation is of interest as indicating a new twinning law for this mineral. It seems probable that the twinning lamellæ may be produced by pressure. B. H. B.

Widespread Occurrence of Allanite as an Accessory Constituent of Rocks. By J. P. Iddings and W. Cross (*Amer. J. Sci.*, **30**, 108—111).—From its mode of occurrence and association, allanite must be added to the group of primary accessory rock constituents, similar to zircon, sphene, and apatite, although much rarer than any of these. In one instance it was noticed enclosing zircon, in others, sphene, apatite, and magnetite. It has, however, also been found in such connection with these minerals as to indicate contemporaneous growth. In some regions, it appears to be uniformly distributed through certain types of rocks, for instance, in the porphyrites of the Ten Mile district, Colorado. On the other hand, near Eureka, Nevada, it seems to be irregularly distributed through a considerable range of rock types. In order to show how extensively allanite is disseminated in minute quantities through a great variety of rocks, the authors note that they have found it microscopically in metamorphic rocks, in older crystalline eruptive masses, and in glassy lavas, in hornblende gneiss and mica gneiss, in granite, quartz porphyry, diorite, porphyrite, andesite, dacite, and rhyolite.

B. H. B.

Artificial Crystallised Lead Silicate. By E. S. Dana and S. L. Penfield (*Amer. J. Sci.*, **30**, 138—139).—The authors have examined a specimen of artificial crystallised lead silicate from the Desloge Lead Company, Bonneterre, Missouri. The hexagonal crystals vary in length and thickness from 1 to 3 mm., and usually exhibit only the planes ∞P and 0P. Rarely, however, the basal edges of the prism are rounded, and in a few cases distinct planes were observed. The length of the vertical axis is $c = 1·032$. Two analyses were made; for the

first (I) only distinct crystals (sp. gr. 5·92) were taken. The result, after deducting 0·44 per cent. of magnetite, is given below. The second (II) was of the crystalline part of the slag. The result is given after deducting 0·207 per cent. of magnetite.

	SiO_2.	PbO.	FeO.	MnO.	CaO.	MgO.	Na_2O.	Total.
I.	17·17	72·39	0·51	—	7·48	0·56	0·35	98·46
II.	16·00	75·26	0·74	0·17	6·15	0·50	0·24	99·06

Both analyses correspond with the formula $R_7Si_4O_{15}$. The occurrence of this rare compound is especially interesting in connection with the discovery of native lead silicates at Långban, Sweden (Abstr., 1879, 22, and 1884, 972). B. H. B.

Analcime from the Phœnix Mine, Lake Superior. By S. L. Penfield (*Amer. J. Sci.*, **30**, 112—113).—The crystals occur thickly grouped together on calcite and native copper, associated with apophyllite and milky quartz. They are of all sizes up to 1 cm. in diameter; the small ones being simply tetragonal trisoctahedra. The larger ones are of the same form, but with the planes differently arranged. Examined in thin section under the microscope, it is seen that all the larger crystals have an opaque centre; the outer portion seeming to be a secondary growth about an older analcime crystal. B. H. B.

The Scapolite, Chabasite, and Phillipsite Groups. By G. Rammelsberg (*Zeit. Kryst. Min.*, **11**, 171—172).—The author is of opinion that Tschermak's law does not hold good in the case of the scapolites (this vol., p. 30). The terminal members of the series assumed by Tschermak, described by him as meionite and marialite silicates, are hypothetical compounds, seeing that true meionite always contains Na, and true marialite always contains Ca. Supported by the results of a number of analyses, the author shows that the ratio $R^{II} : Al_2$ is not, as Tschermak assumes, constant (= 4 : 3), but varies. A new analysis of wernerite from Gouverneur is given, the results being as follows:—

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	Cl.	Total.
52·80	25·07	10·52	8·10	1·53	2·33	100·35

In conclusion, the author opposes the theories of W. Fresenius, that the members of the chabasite-group are a mixture of $R^{II}Al_2Si_2O_8 + 4H_2O$ and $R^{II}Al_2Si_6O_{16} + 6H_2O$, and that the members of the phillipsite, desmine, and harmotome group are mixtures of two terminal members. B. H. B.

Enlargements of Hornblende Fragments. By C. R. Van Hise (*Amer. J. Sci.*, **30**, 231—235).—The enlargement of grains of quartz as first described by Sorby (*Proc. Geol. Soc.*, 1880, 62), has since been shown to explain the consolidation of quartzose sandstones to quartzites. This enlargement consists in the deposition of silica about rolled grains of quartz, the new silica being optically continuous with the old grains. The secondary growth of rolled grains of felspar in

felspathic sandstones in a corresponding manner was also previously noted by the author. He now describes some unmistakable enlargements of hornblende fragments in some peculiar conglomerates from the north-eastern part of Minnesota. B. H. B.

Phillipsite from Brazil. By H. Gorceix (*Zeit. Kryst. Min.*, **11**, 203).—Hitherto apophyllite was the only zeolite found in Brazil. Recently at Abaété, in Minas-Geraës, crystals of a zeolite have been found in cavities in an amygdaloid. The mineral was found on analysis to have the composition of phillipsite (sp. gr. 2·15); the analytical results being as follows:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
I.	47·5	20·6	1·1	7·6	3·1	4·4	0·8	15·0	100·1
II.	46·9	21·5	2·4	7·0	2·3	4·6	1·6	15·0	101·3

B. H. B.

New Locality for Zoisite. By W. H. Bell (*Min. Mag.*, **6**, 109—110; *Zeit. Kryst. Min.*, **11**, 179).—The author found the mineral, which Heddle determined to be zoisite, at Loch Garve, Ross-shire. Analysis gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	CuO.	Total.
43·00	27·73	2·47	24·16	1·40	0·87	trace	99·63

B. H. B.

Staurotide. By Coloriano (*Bull. Soc. Chim.*, **44**, 427—429).—The author proposes the formula $5SiO_2,6Al_2O_3,2FeO,H_2O$ for staurotide, based on the following figures from the analyses of a carefully prepared sample of the mineral:—

FeO.	F_2O_3.	Al_2O_3.	SiO_2.	H_2O.	Total.
9·13	6·83	54·20	27·38	1·43	98·97

He considers that the ferric oxide found is due to the action of the air on the original mineral. A. P.

Occurrence of Fayalite in the Lithophyses of Obsidian and Rhyolite in the Yellowstone National Park. By J. P. Iddings (*Amer. J. Sci.*, **30**, 58—60).—The obsidian, near Beaver Lake, is rich in spherulites, especially of the more or less hollow forms called lithophyses by v. Richtofen. The walls of the cavities in these lithophyses are usually coated with quartz and tridymite. Scattered among them are small, opaque, black crystals, 2 mm. long. Analysis gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Ignition.	Insol.	Total.
25·61	trace	14·92	51·75	1·66	none	none	7·02	100·96

Considering the F_2O_3 as the opaque coating of alteration, and the insoluble silica as the adhering quartz, the composition of the unaltered material will be—

SiO_2.	FeO.	MgO.	Total.
32·41	65·49	2·10	100·00

which is essentially the composition of fayalite.

Perfectly unaltered crystals were subsequently found in small lithophyses in compact obsidian, near the Lake of the Woods. The crystals from both localities are tabular in form, with orthorhombic symmetry; the axial ratio being $a : b : c = 0{\cdot}4584 : 1 : 0{\cdot}5791$. The plane of the optical axes is parallel to the base; one of the bisectrices being normal to the macropinacoid.

Similar crystals of fayalite are found in the lithophyses in rhyolite from several localities in the Yellowstone National Park. Well-developed natural crystals of fayalite have never been found before, although they frequently occur as furnace-products and iron slags.

B. H. B.

Manganese Silicates. By A. Des Cloizeaux (*Zeit. Kryst. Min.*, **11**, 207—208).—Krenner has found that the specimens of Breithaupt's *manganocalcite*, in Vienna and Budapest, are rhombohedral. The author was therefore induced to examine the specimen in the Freiberg Museum. This he finds to be asymmetric, and quite unlike manganocalcite, having in fact the following composition:—

SiO_2.	MnO.	Fe_2O_3.	$CaCO_3$.	H_2O.	Total.
43·07	34·73	1·15	14·59	6·53	100·07

In conclusion, the author gives a description of the optical properties of the following other manganese silicates:—Bustamite, from Mexico and from Longbån, and pajsbergite, from Pajsberg in Sweden.

B. H. B.

Chemical Composition of the Cobalt and Nickel Ores of New Caledonia. By T. B. Readman (*Proc. Roy. Soc. Edin.*, **119**, 65—72).—The surface deposits of cobalt ore are found in the midst of certain aluminous ferruginous masses at low altitudes and not far from the sea; they contain veins of chrome ore. The oxide of cobalt generally forms 3—5 per cent. of the ore mixed with $1\frac{1}{2}$ per cent. of nickel oxide; the silver and chrome vary considerably, 30—1·81 per cent.

The nickel ores which are free from cobalt, exist as double silicate with magnesium, the metal being present to the amount of 10 per cent.

E. W. P.

Meteoric Iron from Trinity Co., California. By C. U. Shepard (*Amer. J. Sci.*, **29**, 469).—The meteorite described was procured ten years ago at Canyon City, in Trinity Co. The first portions detached consisted of limonite containing minute particles of nickeliferous iron. The thickness of the crust affording the limonite was a tenth of an inch; the meteorite consequently must have originated in a very ancient fall. The sp. gr. of the limonite is 3·81 to 4·04. In the nearly unaltered interior the coarsely grained crystallisation was apparent, affording cleavable octahedral crystals similar to what are found in the Putnam iron. The sp. gr. was 7·1. The fact that the sp. gr. is less than the average of meteoric irons is due to the slight

adhesions of hydrated ferric oxide. To the same reason is due the loss in the following analysis:—

Fe.	Ni.	Co.	P.	Total.
88·810	7·278	0·172	0·120	96·380

No sulphur was present. The weight of the mass is 19 lbs. Its shape is oval, with numerous elongated depressions. B. H. B.

Meteoric Iron from Glorieta Mountain, New Mexico. By G. F. Kunz (*Amer. J. Sci.*, **30**, 235—238).—The meteorite described was found in May, 1884, on Glorieta Mountain, near Canoncito, Sante Fé Co. The weight of the mass is 317 lbs. It is in three fragments. The iron is one of the holosiderites of Daubrée, and comes under the general group of caillite of Meunier. It resembles the irons of Augusta Co., Virginia, Whitfield Co., Georgia, and Washington Co., Wisconsin. An analysis of a compact piece of the iron gave the following results:—

Fe.	Ni.	Co.	P.	Total.
87·93	11·15	0·33	0·36	99·77

The investigation is incomplete; facts regarding the included minerals will be published in a subsequent paper. B. H. B.

The Grand Rapids Meteorite. By R. B. Riggs (*Amer. J. Sci.*, **30**, 312).—I. R. Eastman recently described (Abstr., 1885, 494) a meteorite found in Grand Rapids, Michigan. A preliminary analysis was made at the time. A more complete analysis gives the following results:—

Fe.	Ni.	Cu.	Mg.	P.	S.	C (combined).	Graphite.	Total.
88·71	10·69	0·07	0·02	0·26	0·03	0·06	0·07	99·91

The meteorite is a mass of great apparent homogeneity, weighing originally about 50 kilos. B. H. B.

Meteorite of Fomatlán, Jalisco, Mexico. By C. U. Shepard (*Amer. J. Sci.*, **30**, 105—108).—The striking peculiarity of this meteorite, which fell about the end of the year 1883, near the coast in the State of Jalisco, is the prevalence everywhere of octahedral crystals of nickeliferous iron. The mineralogical constitution of the meteorite is approximately as follows:—

Chrysolite	80
Chladnite (?)	10
Nickeliferous iron	7
Troilite, Chromite, Ferric oxide	3
	100

The sp. gr. of the two fragments examined was 3·47 to 3·48.

B. H. B.

Thermo-mineral Waters of Hammam el Lif, Tunis. By A. Barillé (*J. Pharm.* [5], **13**, 14—17).—There are two springs situated on the south coast of the Gulf of Tunis, lat. 36° 44′ N., long. 8° 1′ E. from Paris, about 800 metres from the sea. The *Hammam el Bey* spring (I) has a temperature of 47°, and a density of 1·0116 at 13°; that of *Hammam el Arian* (II) has a temperature of 48°. The composition of the two waters was found to be as follows, in grams per litre:—

	NaCl.	$CaCl_2$.	$CaSO_4$.	$MgSO_4$.	$MgCO_3$.	SiO_2.
I.	8·8417	1·3118	1·4509	0·1053	0·3444	0·065
II.	10·1505	1·5339	1·5963	0·1853	0·3916	0·071

	I. Fe. Al_2O_3. HNO_3.	Total.	Solid residue dried at 180°.
I.	traces	12·0191	12·655
II.	traces	13·9288	14·431

J. T.

Chemistry of Sea Water. By A. Hamberg (*J. pr. Chem.* [2], **33**, 140—150).—Waters collected during Nordenskiöld's expedition to Greenland (1883) at different latitudes and depths, contained varying amounts of salts in solution; but the product obtained by multiplying the percentage of sulphuric anhydride by 100, and dividing by the percentage of chlorine, gave almost constant numbers, 11·52 to 11·45. Waters collected in warmer regions at all depths, and below the surface in cold regions, were found to contain a very slightly lower proportion of sulphates than waters collected at the surface among the ice. This is accounted for by the fact that ice in its formation takes up more chlorides in proportion to sulphates, thus leaving a larger proportion of sulphates in the surrounding water. N. H. M.

Salinity of the Waters of the Firth of Forth. By H. R. Mill (*Proc. Roy. Soc. Edin.*, **119**, 29—64).—This paper is a record of six months' observation of the waters of the Firth of Forth during 1884, and contains a full description of the methods of collection and of analysis, together with full details of results obtained. E. W. P.

Organic Chemistry.

Method of Determining the Purity of Volatile Liquids. By E. Duclaux (*Compt. rend.*, **101**, 1501—1502).—When a known volume of a solution of an alcohol or a volatile fatty acid is distilled and equal fractions are collected, the quantity of alcohol or acid contained in each fraction increases or decreases according to a regular law which is characteristic of the particular substance. The less the volatility of the pure substance, the greater is its volatility in an aqueous solu-

tion. If two or more of these compounds are mixed in the solution, each behaves as if it alone were present, and the nature and approximate proportions of the mixed substances can be deduced from the progress of the numbers representing the composition of the mixture which passes over in the different fractions.

A 1 or 2 per cent. solution of the liquid is divided into two equal parts by distillation, and each half is subjected to fractionation. If the liquid is pure, both portions should behave in precisely the same manner, but if the liquid is a mixture, the first distillation will produce an unequal distribution of the components, and when the two portions are fractionated they will show differences depending on the nature and proportions of the mixed substances.

The author has applied this method to the examination of ordinary samples of the fatty acids. Commercial acetic and formic acids are frequently perfectly pure, propionic acid is somewhat less pure, whilst butyric, valeric, and caproic acids are generally contaminated with higher or lower homologues. The author gives a series of numbers representing the quantities of the different fatty acids which pass over in successive fractions of their pure solutions. C. H. B.

Reduction of Chloropicrin and Dinitrochloromethane. By F. Raschig (*Ber.*, **18**, 3326—3328).—Stannous chloride acts on chloropicrin with formation of cyanogen chloride and hydrogen chloride.

Dinitrochloromethane is prepared by adding 400 c.c. of fuming nitric acid to 200 grams of crude naphthalene tetrachloride, contained in a large retort connected with a well-cooled receiver; when the reaction, which is very violent, ceases, the whole is heated until it begins to froth. The distillate is then diluted with an equal volume of water and steam distilled. The yield is 4 per cent. of the weight of naphthalene tetrachloride. When reduced with stannous chloride, it yields hydroxylamine and ammonium chloride. N. H. M.

Polymeric Trichloracetonitrile. By A. Weddige (*J. pr. Chem.* [2], **33**, 76—90).—Polymeric trichloracetonitrile, $C_3N_3(CCl_3)_3$, has already been obtained (Abstr., 1884, 35) by acting on ethyl paracyanocarbonate with phosphoric chloride. It is best prepared by saturating the ordinary nitrile in portions of 70—80 grams with dry hydrogen chloride, and exposing it to light in sealed tubes as much as possible. The change takes place very slowly, not at all in absence of light, and is not influenced to any extent by heating. The polymeride gradually separates, and is purified by crystallisation from alcohol. It forms long, colourless, transparent prisms, which melt at 96°, and is readily soluble in alcohol, benzene, ether, chloroform, &c. Water at 150—170° does not act on it. It is partly decomposed by hydrochloric acid at 200°. Warm aqueous or cold alcoholic potash converts it into chloroform and cyanuric acid. It is therefore a derivative of trimolecular hydrocyanic acid, and may be described as perchlorotrimethylcyanidine (comp. Pinner, *Ber.*, **18**, 760).

Amidodiperchloromethylcyanidine, $NH_2{\cdot}C_3N_3(CCl_3)_2$, is prepared by dissolving paratrichloracetonitrile in alcoholic ammonia, evaporating,

and washing the residue with water to remove ammonium chloride. It forms colourless, transparent, flat prisms, melting at 165—166°, readily soluble in alcohol, ether, and benzene, sparingly in water. When boiled with aqueous potash, it is decomposed into chloroform and a pulverulent substance, probably ammelide.

Diamidoperchloromethylcyanidine, $C_3N_3(NH_2)_2 \cdot CCl_3$, is obtained by heating the nitrile with alcoholic ammonia at 105—110°. The product is freed from alcohol, treated with water and crystallised from alcohol, from which it separates in long, transparent, lustrous, double pyramids, with alcohol of crystallisation, which they lose on exposure to air, becoming opaque; it also crystallises from alcohol in lustrous hexagonal prisms without alcohol of crystallisation. It melts at 235—236°, and dissolves readily in hot alcohol, sparingly in ether and benzene. The *hydrochloride* (with 2 mols. H_2O) forms large, lustrous plates; it loses hydrochloric acid at 100°. When an excess of ammonia is added to a solution of the hydrochloride, chloroform is formed, and a compound, $C_3N_3(NH_2)_2 \cdot OH$, separates as a white, lustrous, crystalline powder. The *platinochloride* forms long, yellow prisms. The compound can be obtained directly from the polymeric nitrile, by heating it with aqueous ammonia at 120° for 6—8 hours. The author has not yet determined whether it is identical or isomeric with ammeline, from which it differs only in crystalline form.

Methylamidodiperchlorocyanidine, $C_3N_3(CCl_3)_2 \cdot NHMe$, is obtained by evaporating the nitrile with an alcoholic solution of methylamine. It forms small, colourless crystals melting at 115—117°, readily soluble in alcohol and hot benzene. It has no basic properties. The *dimethyldiamide*, $CCl_3 \cdot C_3N_3(NHMe)_2$, is obtained by heating the nitrile with alcoholic methylamine at 110°, and forms small, white crystals melting at 206—207°. It is soluble in alcohol and benzene. Ammonia decomposes the hydrochloride in aqueous solution with formation of chloroform.

Amidomethylamidoperchloromethylcyanidine, $NH_2 \cdot C_3N_3(NHMe) \cdot CCl_3$, is formed when the monamide, $NH_2 \cdot C_3N_3(CCl_3)_2$, is heated with alcoholic methylamine at 110°. It forms small, colourless crystals which melt at 153—155°. It is soluble in alcohol and benzene and forms salts with acids.

When paratrichloracetonitrile is heated at 120° with aqueous methylamine, dimethylamidoperchloromethylcyanidine and a compound identical with that obtained by Hofmann, by the action of methylamine on cyanuric chloride (this vol., p. 38) are formed.

N. H. M.

Cyanuric Acid, Di- and Tri-thiocyanuric Acids. By P. Klason (*J. pr. Chem.* [2], **33**, 116—132).—Trithiocyanuric acid (Abstr., 1885, 1194) is prepared by gently warming a concentrated aqueous solution of potassium hydrogen sulphide (4 mols.) with cyanuric chloride (1 mol.). The acid does not melt when heated, but volatilises at a dull red heat without carbonising. When heated at 360° it yields *melene*, $C_6H_6N_{10}$. This forms a grey powder. *Potassium trithiocyanurate*, $C_3N_3S_3K_3 + 3H_2O$, and several other metallic salts were prepared. The ethyl salt forms large, colourless plates, without odour, melting at 27°, readily soluble in ether, &c.; it boils at about

350°. The *amyl salt* is a thick oil; the *phenyl salt* crystallises in splendid lustrous prisms melting at 97°: the *paratolyl salt* melts at 114°.

Iodine acts on tricyanuric acid dissolved in ammonium carbonate with formation of *cyanuric bisulphide*, $(C_3N_3)_2S_6$. This is decomposed by hydrochloric acid into cyanuric acid, sulphur, and hydrogen sulphide.

Cyanuric trithioglycollic acid, $C_3N_3(SCH_2{\cdot}COOH)_3$, is obtained by heating ethyl sulphocyanacetate, or by the action of the tertiary potassium trithiocyanate on potassium chloracetate. When boiled with hydrochloric acid, it is decomposed into cyanuric and glycollic acids.

Dithiocyanuric acid, $OH{\cdot}C_3N_3(SH)_2 + H_2O$, is best obtained by evaporating an alcoholic solution of potassium thiocyanate at 30—40°. The viscous, brownish-yellow mass so formed is treated with strong ammonia, filtered, and barium chloride added to the filtrate. It is soluble in boiling water and in alkalis. Concentrated hydrochloric acid at 100° decomposes it into cyanuric acid and hydrogen sulphide. Salts are described.

Hydroxycyanuric bisulphide, $OH{\cdot}C_3N_3 : S_4 : C_3N_3{\cdot}OH$, is obtained by treating a cold dilute solution of dithiocyanuric acid with iodine solution. It forms microscopic, well-formed, white, lustrous octahedra. Boiling water decomposes it into sulphur, hydrogen sulphide, and cyanuric acid.

The author discusses the various formulæ ascribed to cyanuric acid and to dicyandiamide, and considers that the constitutional formula $NH{\cdot}_2C\langle^{N}_{N}\rangle C{\cdot}NH_2$ would account for all the reactions of the latter compound (compare Rathke, this vol., p. 217).

Normal methyl cyanurate was prepared by the action of sodium methoxide on cyanuric chloride, and is identical with that prepared by polymerization. Ethyl cyanurate was prepared in the same way; it melts at 29°, and boils at 275° (compare Ponomareff, Abstr., 1882, 937). It is also formed, together with the iso-compound, from silver cyanurate and ethyl iodide. Amyl cyanurate was obtained from cyanuric chloride and sodium amyl oxide, and forms a colourless oil, without odour, boiling at 360° with little decomposition; it is therefore not identical with Hofmann's compound, which boils at 200°. Phenyl cyanurate was prepared in a similar manner, and is identical with the compound obtained by polymerization. N. H. M.

Rhodanic Acid. By J. Ginsburg and S. Bondzynski (*Ber.*, **19**, 113—124).—Continuing the work of Nencki and Bourquin (Abstr., 1885, 40), the authors have further investigated the non-nitrogenous acid formed by the action of alkalis on rhodanic acid, and also the condensation-products of rhodanic acid with benzaldehyde (*loc. cit.*).

The non-nitrogenous acid crystallises in scales, easily soluble in water, alcohol, and ether, and sparingly so in boiling benzene. It forms a crystalline *potassium salt*, $C_4H_4K_2O_4S_2 + 1\frac{1}{2}H_2O$, and a white *silver salt*, $C_4H_5AgO_4S_2$. This *glycollic acid bisulphide* undoubtedly

has the formula $COOH{\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2{\cdot}COOH$. When heated with tin and hydrochloric acid, it yields thioglycollic acid, $SH{\cdot}CH_2{\cdot}COOH$; this is very readily reoxidised, even a solution of its potassium salt being converted into the bisulphide-glycollate, when heated in contact with the air. By acting on the rhodanic acid with baryta (barium thioglycollate is insoluble), instead of potash, thioglycollic acid is obtained in place of glycollic acid bisulphide. The latter is therefore a secondary product formed during the evaporation of the alkaline solution. Ferric chloride very rapidly converts thioglycollic acid into the bisulphide acid, and this reaction may be used for the quantitative determination of thioglycollic acid. The decomposition of rhodanic acid, therefore, takes place according to the equation $SH{\cdot}CH_2{\cdot}CO{\cdot}S{\cdot}CN + H_2O = SH{\cdot}CH_2{\cdot}COOH + HSCN$. If baryta is employed, this reaction gives an easy means of obtaining pure thioglycollic acid.

Benzylidene-rhodanic acid was heated with excess of concentrated sulphuric acid at 110°, until a test quantity gave scarcely any precipitate on dilution with water. A syrupy acid was thus obtained, which gradually deposited large, flexible needles. It is so excessively soluble in alcohol and water, that it could not be obtained pure in the free state. Crystalline *sodium*, *potassium*, and *ammonium salts* were obtained, having the formula $R{\cdot}C_{10}H_6NS_2O_5$. The acid has one of the three following formulæ:

$$OH{\cdot}CPh : C(SO_3H){\cdot}CO{\cdot}S{\cdot}CN,$$
$$OH{\cdot}C_6H_4{\cdot}CH : C(SO_3H){\cdot}CO{\cdot}S{\cdot}CN, \text{ or } SO_3H{\cdot}C_6H_4{\cdot}CH : C(OH)CO{\cdot}S{\cdot}CN.$$

The authors are inclined to think the third the most probable. When the sodium salt of this acid is boiled with nitric acid (of sp. gr. 1·22) two mononitro-derivatives, $C_{10}H_5NS_2O_5Na{\cdot}NO_2$, are obtained. One crystallises with 1 mol. H_2O in snow-white needles, easily soluble in alcohol, sparingly in water, and decomposes at 100—105°; the other forms anhydrous, pale-yellow needles, more easily soluble in water, but less so in alcohol, and remains unchanged at 110—115°. When heated with baryta, benzylidene-rhodanic acid yields thiocyanic acid, and *hydrothiocinnamic acid*, $CHPh : C(SH){\cdot}COOH$, a pale-yellow substance, melting at 119°, and easily soluble in alcohol, ether, benzene, and carbon bisulphide; almost insoluble in water. An alcoholic solution is converted by iodine into a substance crystallising in long, yellow needles melting at 179°. It probably has the formula $CHPh : C(COOEt){\cdot}S{\cdot}S{\cdot}C(COOEt) : CHPh$.

The authors are examining the action of hydrobromic acid on hydrothiocinnamic acid, in the hopes of obtaining a substituted cysteïn.

L. T. T.

Homologue of Rhodanic Acid. By J. Berlinerblau (*Ber.*, **19**, 124—126).—By heating α-chloropropionic acid with a concentrated solution of ammonium thiocyanate, the author obtained a methylrhodanic acid, $SH{\cdot}CHMe{\cdot}CO{\cdot}S{\cdot}CN$, crystallising from boiling water in long pale-yellow needles, melting at 123°. The author is studying the products of hydrolysis. He is also investigating the condensation-

product of methylal with rhodanic acid, with the view of synthesising cysteïn. L. T. T.

Products of the Slow Combustion of Ethyl Ether. By L. Legler (*Ber.*, **18**, 3343—3351; compare Abstr., 1881, 576).—When ether is slowly burned by means of slightly glowing platinum foil, *hexahydroxymethylene peroxide*, $(CH_2O)_6O_3 + 3H_2O$ (to which the formula $C_{11}H_{33}O_{21}$ was previously ascribed), is formed. Ammonia acts on it with evolution of oxygen and formation of ammonium formate, hexamethylenamine and *hexahydroxymethylenediamine*, $(CH_2O)_6N_2$. The latter crystallises partly in cubes. When slightly heated, it gives off an odour of cheese; when strongly heated, it detonates with formation of hydrocyanic acid. It is sparingly soluble in water, alcohol, and ether; dilute acids dissolve it with formation of hexahydroxymethylene peroxide. On further heating the acid solution, formic acid, aldehyde, and an ammonium salt of the acid employed, are obtained.

When hexahydroxymethylene peroxide is treated with soda solution it is decomposed into aldehyde, formic acid, and hydrogen. When 1 gram of the substance was distilled with dilute sulphuric acid, 0·21 gram aldehyde and 0·598 gram formic acid were obtained.

A very delicate test for hexamethylenediamine consists in adding bromine-water, which precipitates an orange-yellow substance; this, when exposed to air, loses bromine, and there remains a sulphur-coloured compound, $(CH_2)_6N_4Br_2$, crystallising in prisms.

N. H. M.

Preparation of Amyl Nitrite. By J. Williams and M. H. Smith (*Pharm. J. Trans.* [3], **16**, 499—501).—The gases evolved by the action of various strengths of nitric acid on arsenious anhydride were passed into amyl alcohol (kept cool) until the alcohol became brownish-green in colour. The quantity of absorbable gas produced, and the energy of the absorption decreased with the strength of the acid employed; on the other hand, the percentage of the product distilling below 100° increased under the same circumstances; and as amyl nitrite boils somewhere about 95—96°, this fact is important. For example, nitric acid of 1·500 sp. gr. produced a gas almost entirely, and very energetically, absorbed, but only 42 per cent. of the liquid produced distilled below 100°; whilst with acid of 1·300 sp. gr. only a very small percentage of the gas produced was absorbed, but 93 per cent. of the product distilled below 100°. Intermediate strengths are intermediate in their activity, acid of sp. gr. 1·350—1·360 being the best for the purpose. When the gases from the action of nitric acid on copper and from 1·520 nitric acid on arsenious anhydride are mixed, the former in large excess, and passed into amyl alcohol, as in the other experiments, much gas is absorbed, and the liquid produced contains 95 per cent. distilling below 100°. D. A. L.

Oxidation of Glycerol in Alkaline Solution: Preparation of Pure Glyceric Acid. By E. Börnstein (*Ber.*, **18**, 3357—3358).—When mercuric oxide and barium hydroxide are added to a strong

boiling aqueous solution of glycerol, as long as any action takes place, the product filtered, evaporated and the barium salt thus obtained decomposed by sulphuric acid, a solution of almost pure glyceric acid is obtained. The yield is 45 per cent. of the weight of glycerol employed. N. H. M.

Oxidation of Levulose. By E. Börnstein and A. Herzfeld (*Ber.*, **18**, 3353—3357).—When an aqueous solution of levulose is heated at 100° with mercuric oxide and a small quantity of baryta, formic and glycollic acids and *normal trihydroxybutyric acid*, $C_4H_8O_5$, are formed. The latter compound forms a thick syrup. When reduced it yields a lactone. The *calcium salt* (with 4 mols. H_2O) and *barium salt* were prepared. These results make it probable that levulose has the constitution $OH{\cdot}CH_2{\cdot}CO{\cdot}[CH(OH)]_3{\cdot}CH_2OH$ (compare this vol., p. 220). N. H. M.

Action of Bromine and Water on Levulose. By M. Hönig (*Ber.*, **19**, 171—172).—Börnstein and Herzfeld have found the main product of the oxidation of levulose with mercuric oxide to be trihydroxybutyric acid (preceding Abstract). The author had independently arrived at a similar result, using aqueous bromine as the oxidising agent. A. J. G.

Preparation of Galactose. By E. Bourquelot (*J. Pharm.* [5], **13**, 51—54). — Stoppered flasks of 600 c.c. capacity are charged with 100 grams of milk-sugar, 9 grams of sulphuric acid, and water to make up 600 c.c. The stoppers were wired in, and the flasks are heated at 105° in a calcium chloride bath for one hour, and then cooled. After neutralising with barium carbonate and filtering, the solution is evaporated until the liquid corresponding with 500 grams of milk-sugar weighs 640 grams. The syrup is set aside to crystallise, and this is completed in 4—5 days if a little galactose previously prepared be added to it. A little alcohol at 80° is then added and the crystals are drained. This treatment is repeated, when a very white product is obtained. From 500 grams of milk-sugar, 120 to 135 grams of galactose dried at 108° are obtained. 250 grams of the crystals are heated with 180 c.c. boiling water and 1 litre of alcohol at 90°, in a reflux apparatus for 20 minutes. All the crystals dissolve; after filtering, the crystals soon begin to appear again, and in 24 hours about 150 grams are obtained. These crystals have the form of hexagonal plates. After drying at 100°, they fuse at 163—164°, and after repeated crystallisation, show a rotatory power of $[\alpha]_D = 80° 74'$ at 19°.
J. T.

Decolorisation of Iodide of Starch by Heating. By C. Tomlinson (*Phil. Mag.* [5], **20**, 168—171).—After alluding to the many but discrepant observations on the decolorisation of the so-called iodide of starch on heating, and the return of the colour on cooling, the author describes experiments made with different samples of starch from maize, rice, sago, and potato. It was found that the blue colour in all cases disappeared at the temperature of

boiling water, although the actual temperature of decolorisation varied according to the nature of the starch. The colour was not in any case reproduced on cooling, provided that the boiling be carried on for a sufficiently long time, a process protected by the greater solvent power of the liquid for iodine with increase of temperature (compare Brukner, Abstr., 1884, 575). Owing to the formation of a minute quantity of hydriodic acid, the blue colour can be restored on the addition of chlorine to the cooled liquid. V. H. V.

Glucosamine. By F. Tiemann (*Ber.*, **19**, 49—53; compare Abstr., 1884, 724).—When glucosamine hydrochloride in aqueous solution is treated with phenylhydrazine, it yields phenylglucosazone, a substance obtained by E. Fischer by the action of phenylhydrazine on dextrose or levulose (Abstr., 1885, 53).

Glucosamine hydrobromide, $C_6H_{13}NO_5$,HBr, is readily obtained by the action of concentrated hydrobromic acid on chitin; it crystallises in large, white, seemingly monosymmetric prisms, dissolves readily in water, sparingly in alcohol, and is insoluble in ether. Chitin is also dissolved by hydriodic acid, but on evaporation the solution is decomposed with separation of iodine.

Landoldt has made determinations of the rotatory power of aqueous solutions of glucosamine hydrochloride, and confirms Ledderhose's statement that the rotatory power increases with the concentration; thus a 5·16 per cent. solution gives $[\alpha]_D = +74·64$, whilst a 2·6 per cent. solution gives only $[\alpha]_D = 70·61$. A. J. G.

Specific Rotatory Power and Crystalline Form of Glucosamine Hydrobromide. By F. Tiemann (*Ber.* **19**, 155—157).—Glucosamine hydrobromide (preceding Abstract) shows a specific rotatory power increasing with the increase of dilution of the solution. Thus for a 22·555 per cent. solution $[\alpha]_D = 59·37$; 12·505 per cent. solution $[\alpha]_D = 59·63$; and for a 5·312 per cent. solution $[\alpha]_D = 60·23$. This may be expressed by the general formula $[\alpha]_D = 55·21 + 0·053053q$, where q = the percentage of water in the solution.

It crystallises in the monosymmetric system:

$$a : b : c = 1·5889 : 1 : 0·7786;\ \beta = 85°\ 30'.$$

Observed faces $\infty\breve{P}\infty$, $+\breve{P}\infty$, $+3\breve{P}\infty$, $\infty P2$, $-P$, $+P$. It is isomorphous with the hydrochloride. A. J. G.

Alkylene Diamines. By A. T. Mason (*Ber.*, **19**, 112—113).—By mixing together ethylenediamine and phenanthraquinone in warm acetic solution, the author has obtained a substance, $C_{16}H_{12}N_2$, crystallising from boiling alcohol in pale-yellow needles, melting at 180·5°, and distilling at a higher temperature without decomposition. The constitution of this substance is most probably

$$\begin{array}{l} C_6H_4{\cdot}C : N{\cdot}CH_2 \\ | \quad\quad | \\ C_6H_4{\cdot}C : N{\cdot}CH_2 \end{array}.$$

Ethylenediamine reacts in similar manner with benzil, benzo-

quinone, sodium dioxytartrate, &c. These reactions and similar ones with diethylenediamine are now being studied. L. T. T.

Guanidine Thiocyanate. By R. Engel (*Bull. Soc. Chim.*, **44**, 424).—Guanidide thiocyanate is not deliquescent as is usually stated, but is unctuous to the touch and very soluble in water, its solubility increasing rapidly with the temperature; 100 parts of water dissolve 73 parts of the salt at 0° and 134·9 parts at 15°; it is soluble to any extent in boiling water, the boiling point of the solution being considerably above 120°, which is the melting point of the salt. By saturating water at 30·5° with the salt, the temperature is reduced to 4°, and the temperature of water at 15·5° is reduced to 3°.

A. P.

Derivatives of Formaldehyde. By C. Wellington and B. Tollens (*Ber.*, **18**, 3298—3311).—The formaldehyde was prepared as already described (Abstr., 1882, 1277). *Anhydroformaldehydephenylhydrazine*, $C_{15}H_{16}N_4$, is obtained by adding 1·54 grams of phenylhydrazine to 736 c.c. of 1·2 per cent. crude formaldehyde. After some time crystals separate. In eight hours the solution is filtered, and the crystals dried over sulphuric acid. The solution may be treated several times with phenylhydrazine until no more crystals separate. It crystallises from alcohol and toluene (mixed) in rhombic plates, melting at 183—184°. It is analogous to hexamethylenamine (Abstr., 1884, 988).

Anhydroformaldehydeparatoluidine, $(C_7H_7{\cdot}NCH_2)_n$, is formed by acting on formaldehyde with toluidine. Two substances were obtained having the same composition; the one is readily soluble in toluene and melts at 122°, the other is sparingly soluble. Its melting point varied from 205° to 238°. When heated with dilute sulphuric acid, both compounds give off the odour of formaldehyde.

Anhydroformaldehydeorthotoluidine, $(C_7H_7{\cdot}NCH_2)_n$, is obtained by the action of formaldehyde on orthotoluidine; it forms an almost colourless oil, which gradually becomes brown and syrupy.

When anhydroformaldehydeaniline (*loc. cit.*) is crystallised from a mixture of toluene and alcohol, a sparingly soluble substance melting at about 172° remains undissolved; whilst the solution yields white needles, having the same melting point (138°) as before. It is identical with Pratesi's dimethylenediphenyldiamine (Abstr., 1885, 782). α- and β-Naphthylamine and xylidine also yield compounds with formaldehyde. N. H. M.

Iodaldehyde. By P. Chautard (*Compt. rend.*, **102**, 118—120).—50 grams of iodine, 20 grams of crystallised iodic acid, and 150 c.c. of a 30 per cent. aqueous solution of aldehyde are mixed and allowed to remain in a closed flask until the iodine is completely dissolved. About 500 c.c. of water is then added, and the iodaldehyde separates in a heavy, oily layer. The reaction is complete in three or four days at the ordinary temperature, or in a few hours if the mixture is gently heated. If pure aldehyde is used, there is considerable development of heat, and resinous products, which probably contain polymerides, are formed.

The crude product is dissolved in ether, agitated with pure mercury to remove excess of iodine, and dried in a vacuum over sulphuric acid.

Iodaldehyde is a colourless, limpid, oily liquid, which blackens rapidly when exposed to light, and does not solidify at $-20°$; sp. gr. at $20° = 2{\cdot}14$. It is non-inflammable and volatile, but decomposes at 80°, and cannot be distilled without decomposition, even under a pressure of 20 mm. The solutions may, however, be heated to a high temperature without undergoing alteration. Iodaldehyde is soluble in all proportions in alcohol, ether, benzene, chloroform, and carbon bisulphide. It is also soluble to a certain extent in cold water, by which it is not decomposed.

Potash and soda rapidly convert iodaldehyde into iodoform. Sodium hydrogen sulphite combines with it with development of heat, forming a crystalline compound. Aqueous ammonia at the ordinary temperature produces different oxaldines, according to the relative proportions, oxytrialdine and oxypentaldine being the most easily obtained. The latter is also easily prepared by the action of iodine and iodic acid on aldehyde-ammonia at the ordinary temperature. The action of dry ammonia gas on an alcoholic or ethereal solution of iodaldehyde has not yet been fully investigated.

Iodaldehyde is instantly decomposed by dilute acids. Chlorine and bromine displace the iodine, forming chloro- or bromo-derivatives. Nascent hydrogen reconverts it into aldehyde. Aniline, toluidine, and other compound ammonias readily unite with it.

If dry powdered potassium cyanide is added to a solution of iodaldehyde in absolute ether, heat is developed, potassium iodide is precipitated, and cyanaldehyde, $CN{\cdot}CH_2{\cdot}COH$, is formed. This is a colourless, somewhat oily liquid, with a strong odour of nuts. It boils at about 100°, and its vapours produce violent headache.

C. H. B.

Action of Potassium Chlorate on Chloral Hydrate. By K. Seubert (*Ber.*, **18**, 3336—3339). — When 165 grams of chloral hydrate and 37·43 grams of potassium chlorate are finely powdered and exposed to direct sunlight in a flask fitted with a reflux condenser, a reaction soon begins with great rise of temperature and the flask must be cooled by immersion in cold water. Chlorine, phosgene gas, carbonic anhydride, and chloroform are given off. In four days the reaction is complete, and a separation of crystals takes place which may be increased by surrounding the flask with ice. The whole is then filtered and washed with absolute alcohol. Water is added to the alcoholic solution, which then yields on evaporation very pure hydrogen potassium trichloracetate. A small quantity of perchlorethane is also formed in the reaction.

N. H. M.

Ammonia as a Reagent for Certain Double Ketones. By L. Knorr (*Ber.*, **19**, 46—49).—The syntheses of pyrroline-derivatives by the action of ammonia or of primary amines on diacetosuccinates, acetophenoneacetone, acetonylacetone, and acetophenoneacetoacetates has shown this condensation to be general with diketones of the formula $R{\cdot}CO{\cdot}CHR{\cdot}CHR{\cdot}CO{\cdot}R$ (R standing for any like or unlike radicle).

As all pyrroline-derivatives impart a red colour to pine-wood, the author has devised the following test to ascertain if a diketone has this constitution :—The substance is dissolved in glacial acetic acid, a solution of ammonia in excess of acetic acid is added, and the mixture boiled for half a minute; dilute sulphuric acid is added and the liquid again boiled, while a splinter of pine-wood is immersed.

Ethyl α-β-diacetoglutarate is prepared by boiling ethyl bromolevulinate with an equivalent amount of ethyl sodacetoacetate in alcoholic solution; it was only obtained in an impure state and then boiled at 240—250° under 140 mm. pressure. As it readily shows the reaction above described, it must have either the constitutional formula $COOEt\cdot CH_2\cdot CH(COMe)\cdot CH(COMe)\cdot COOEt$ or

$$COOEt\cdot CH_2\cdot CH_2\cdot CO\cdot CH_2\cdot CH(COMe)\cdot COOEt;$$

the last would, however, require a rather improbable formula for bromolevulinic acid. It may be assumed that the first is correct, and that the bromine-atom occupies the β-position in bromolevulinic acid.

Ethyl carboxydimethylpyrrolylacetate, $COOEt\cdot C_4NHMe_2\cdot CH_2\cdot COOEt$ [Me : $CH_2\cdot COOEt$: COOEt : Me = 2 : 3 : 4 : 5], is obtained by boiling ethyl diacetoglutarate dissolved in acetic acid with excess of ammonium acetate; it crystallises in lustrous plates, melts at 109—110°, is readily soluble in alcohol, chloroform, benzene, and ether, and insoluble in water, alkalis, and dilute acids. The free acid, $C_9H_{11}NO_4$, obtained by saponification of the ethyl salt, crystallises in slender needles, and melts at 196° with evolution of carbonic anhydride and conversion into a red oil, probably 2 : 3 : 5 trimethylpyrroline.

A. J. G.

Behaviour of the Alkaline Hydrosulphides with Alkyl Salts. By C. Göttig (*J. pr. Chem.* [2], **33**, 90—94).—When ethyl acetate is boiled with an alcoholic solution of potassium (or sodium) hydrosulphide, hydrogen sulphide, potassium (or sodium) acetate, and thiosulphate, are formed. The reaction also takes place when ethyl acetate and potassium hydrosulphide are heated together in sealed tubes; the reaction is, however, less complete, owing to the hydrogen sulphide not being able to escape as it is formed.

N. H. M.

Manganese Cyanacetate. By R. Engel (*Bull. Soc. Chim.*, **44**, 425—426).—*Manganese cyanacetate*, $(CN\cdot CH_2\cdot COO)_2Mn + 2H_2O$, is obtained in well-formed crystals; it loses its water of crystallisation at 100°.

A. P.

Decomposition of Trichloracetic Acid and its Potassium Salt by Water. By K. Seubert (*Ber.*, **18**, 3339—3343).—Water at 100° converts trichloracetic acid (and its acid and normal potassium salts) into chloroform and carbonic anhydride (or potassium carbonate). This accounts for the susceptibility of solutions of these salts to decomposition on evaporation.

N. H. M.

Thio-derivatives of Butyric, Isobutyric, and Isovaleric Acids. By J. M. Lovén (*J. pr. Chem.* [2], **33**, 101—115; comp.

Abstr., 1885, 241).—*α-Thiodibutyric acid*, $S(C_3H_6{\cdot}COOH)_2$, is prepared by adding ethyl bromobutyrate (2 mols.) to a solution of potassium hydrogen sulphide (1 mol.) and potassium hydroxide (1 mol.) in alcohol, and subsequently heating the whole on a water-bath. On the addition of water, ethyl thiodibutyrate separates as a heavy oil. The free acid forms groups of needles with a silky lustre, melting at 105°, and very soluble in hot water. The *barium salt*, $C_8H_{12}SO_4Ba$, resembles barium thiodilactate; it is very insoluble. When thiodibutyric acid is neutralised with soda, and heated with 1 per cent. solution of potassium permanganate at 100°, sulphonedibutyric acid, identical with the acid obtained from sulphonediacetic acid, sodium ethoxide, and ethyl iodide (*loc. cit.*) is formed. This is fresh evidence in favour of the constitution ascribed to the substitution-products from bromine and butyric acid.

Thiodiisobutyric acid, $S(CMe_2{\cdot}COOH)_2 + H_2O$, is obtained in a manner similar to thiobutyric acid. It forms large plates, very readily soluble in hydrochloric and acetic acids, sparingly soluble in hot water. The *barium salt* (with 2 mols. H_2O) is readily soluble in hydrochloric and acetic acids, sparingly soluble in hot water. When oxidised with potassium permanganate, it yields sulphonediisobutyric acid, melting at 182—186°, probably identical with the acid obtained from sulphonediacetic acid. Thioacetonic acid is also formed in the preparation of thiodiisobutyric acid.

Thiodiisovaleric acid, $S(C_4H_6{\cdot}COOH)_2$, is prepared in a similar manner to the acids above described. It forms small, lustrous crystals soluble in water.

Sulphonediisovaleric acid, $SO_2(C_4H_6{\cdot}COOH)_2$, is obtained by heating an alcoholic solution of sodium ethoxide (2 mols.), ethyl sulphonediacetate (1 mol.), and isopropyl iodide (2 mols.) at 120° for some hours. The product is treated with water and extracted with ether. The acid is an oil. The *barium salt* (with 7 mols. H_2O) crystallises in groups of needles with a silky lustre, sparingly soluble in water. The acid was also prepared by oxidising thiodiisovaleric acid with potassium permanganate. N. H. M.

Synthesis of Ethyl Acetoacetate from Cyanacetone. By S. W. James (*Annalen*, **231**, 245—248).—The author has repeated the experiments of Matthews and Hodgkinson (Abstr., 1883, 311), but failed to detect the formation of ethyl acetoacetate by the action of hydrochloric acid or of alkalis on cyanacetone. W. C. W.

Action of Carbonyl Chloride on Ethyl Cupracetoacetate. By M. Conrad and M. Guthzeit (*Ber.*, **19**, 19—26).—Ethyl cupracetoacetate is best prepared by mixing a very dilute aqueous solution of copper acetate or sulphate with a mixture of equal volumes of ethyl acetoacetate and alcohol, and then slowly adding the calculated quantity of aqueous ammonia.

Ethyl dehydrodiacetylacetonedicarboxylate, $O<\begin{matrix}CMe{:}C(COOEt)\\CMe{:}C(COOEt)\end{matrix}>CO$, is prepared by slowly adding carbonyl chloride dissolved in benzene

to ethyl cupracetatoacetate placed under benzene. It is crystalline, melts at 79—80°, is soluble in ether, readily soluble in benzene, alcohol, glacial acetic and concentrated sulphuric and hydrochloric acids, and is nearly insoluble in water. With potash, it gives a yellow coloration similar to that given by ethyl chelidonate and other related compounds.

Ethyl dimethylpyridonedicarboxylate (lutidondicarboxylate),

$$NH<\begin{matrix}CMe : C(COOEt)\\CMe : C(COOEt)\end{matrix}>CO,$$

is obtained by the action of concentrated aqueous ammonia on the dehydro-compound. It crystallises in colourless, lustrous well-formed prisms, melts at 221°, is sparingly soluble in boiling water, cold alcohol, ether, carbon bisulphide, and benzene, readily in chloroform, glacial acetic acid, and hot alcohol, and is moderately soluble in hydrochloric and sulphuric acids. It has feeble basic properties; the *platinochloride*, $(C_{13}H_{17}NO_5)_2,H_2PtCl_6$, crystallises in large, orange-yellow needles.

Ethyl trimethylpyridondicarboxylate, $NMe<\begin{matrix}CMe : C(COOEt)\\CMe : C(COOEt)\end{matrix}>CO,$ obtained by the action of methylamine on an acetic acid solution of the dehydro-compound, crystallises in stellate groups of needles, melts at 193°, and is sparingly soluble in cold, more readily in hot water and in alcohol.

Ethyl phenyldimethylpyridondicarboxylate,

$$NPh<\begin{matrix}CMe : C(COOEt)\\CMe : C(COOEt)\end{matrix}>CO,$$

prepared with aniline in a similar manner, is crystalline, melts at 170—171°, and is sparingly soluble in hot water, readily soluble in alcohol and boiling benzene, and in concentrated acids. The *platinochloride*, $(C_{19}H_{21}NO_5)_2,H_2PtCl_6$ is obtained as an orange-yellow, crystalline precipitate, and melts at about 120°. A. J. G.

Ethyl Propiopropionate. By A. Israel (*Annalen*, **231**, 197—234).—Ethyl propiopropionate prepared by a modification of the process originally employed by its discoverers, Oppenheim and Hellon (*Ber.*, **10**, 699), is a colourless liquid of aromatic odour. It boils at 199°, and its sp. gr. at 15° is 0·9870. It is decomposed by ammonia, yielding an amide, $C_6H_{15}NO_2$, which is insoluble in water, and a hygroscopic crystalline substance which melts at 75°. The latter is probably a mixture of $C_6H_{11}NO_2$ and $C_6H_{12}N_2O$. The insoluble amide boils at 195°. It is decomposed by acids, forming ethyl propiopropionate. By the action of bromine on ethyl propiopropionate diluted with absolute ether, ethyl mono- and di-propiopropionates are obtained. The former is a reddish-yellow liquid, sp. gr. 1·337 at 15°. The latter is a yellow liquid, sp. gr. 1·611 at 15°. On treatment with metallic sodium, the monobromo-compound yields a thick oily liquid, boiling between 240° and 260°. It has the composition $C_{16}H_{24}O_6$. The dibromo-compound is decomposed by alcoholic ammonia,

yielding ammonium bromide, and a substance having the composition $OH{\cdot}C_8H_{12}O_3{\cdot}NH_2$.

Ethyl propiopropionate is decomposed by sodium hydroxide, yielding diethyl ketone, alcohol, and sodium hydrogen carbonate.

On treatment with ethyl iodide and sodium ethoxide, ethyl propiopropionate yields ethyl propionate methylethylacetate. The ethylic salt of ethylpropiopropionic acid was not formed. This compound can, however, be obtained by the action of ethyl iodide on a mixture of ethyl propiopropionate and benzene, in which sodium has been dissolved. It is a liquid boiling at 205—207°. Its sp. gr. at 15° is 0·966. It has an odour like that of peppermint. Ethyl propiopropionate is decomposed by alcohol in the presence of a small quantity of sodium alcoholate, yielding ethyl propionate, ketones, and other products.

W. C. W.

Lead Glycollate Chloride. By R. Engel (*Bull. Soc. Chim.*, **44**, 424—425).—This compound, $OH{\cdot}CH_2{\cdot}COOPbCl$, may be readily prepared by adding freshly precipitated and well-washed lead chloride to a solution of ammonium glycollate; it crystallises in colourless groups of needles.

A. P.

Oxidation of Sebacic Acid. By H. Carette (*Compt. rend.*, **101**, 1498—1501).—Sebacic acid was oxidised by means of neutral potassium permanganate, acid potassium permanganate, and nitric acid. In all three cases, the result was the same, the products being succinic acid, adipic acid, and the isopyrotartaric or normal propylenedicarboxylic acid described by Reboul (Abstr., 1879, 133).

C. H. B.

Refractive Power of Organic Compounds. By J. Kanonnikoff (*J. pr. Chem.*, **32**, 497—523).—By comparing the refraction equivalents of itaconic, citraconic, and mesaconic acids as experimentally obtained, with the equivalents indicated by theory, the author finds that itaconic acid does not contain any doubly-linked carbon, and probably has the constitution $CH_2\begin{cases}CH{\cdot}COOH\\ |\\ CH{\cdot}COOH\end{cases}$, whilst mesaconic and citraconic acids both contain doubly-linked carbon, and their constitution may be represented by the formulæ $COOH{\cdot}CMe : CH{\cdot}COOH$ for mesaconic acid, and $CH_2 : C(COOH){\cdot}CH_2{\cdot}COOH$ for citraconic acid; this view is also supported by the fact that Aarland has observed (this Journ., 1873, 377, 1221) that isoallylene is formed when the potassium salt of itaconic acid is electrolysed, whilst citraconic and mesaconic acids yield allylene when treated in a similar manner.

Quinic acid and quercitol also contain no doubly-linked carbons, and their constitution may be represented by the formulæ $CH_2<\begin{matrix}CH(OH){\cdot}CH(OH)\\ CH(OH){\cdot}CH(OH)\end{matrix}>CH{\cdot}COOH$ for quinic acid, and

$$OH{\cdot}CH<\begin{matrix}CH(OH){\cdot}CH(OH)\\ CH(OH){\cdot}CH(OH)\end{matrix}>CH_2 \text{ for quercitol.}$$

An exhaustive examination of the refraction equivalents of the

camphors and terpenes, by comparison among themselves, and with isomeric and allied compounds of known constitution leads the author to adopt the following formulæ for camphor, $CPr\begin{<}\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CH_2\end{matrix}\begin{>}CMe$; and borneol, $CPr\begin{<}\begin{matrix}CH_2\cdot CH(OH)\\ CH_2 \text{ —— } CH_2\end{matrix}\begin{>}CMe$; and analogous formulæ for menthone, menthol, and monobromo-camphor. The formula assigned to terpene is $CPr\begin{<}\begin{matrix}CH:CH\\ CH_2\cdot CH_2\end{matrix}\begin{>}CMe$, to isoterpene, $CPr\begin{<}\begin{matrix}CH\cdot CH\\ CH_2\cdot CH_2\end{matrix}\begin{>}CMe$, and analogous formulæ are given for cajputene monohydrate, lævoterpene hydrate, terpene monohydrochloride, terpin (anhydrous), and tetrahydroterpene. A. P.

Telluryl Tartrates and Citrates. By D. Klein (*Compt. rend.*, **102**, 47—49).—Tellurium yields double tartrates and citrates which in some respects are analogous to tartar emetic. They lose a molecule of water of constitution at 200°, and are really salts of the radicle telluryl, TeO. *Potassium telluryl tartrate* or *potassium tartrotellurite*, $(C_4H_4O_6)_2K_2TeO + H_2O$, is obtained by dissolving equal molecular proportions of tartaric acid and potassium tellurite in water, and concentrating the solution at a gentle heat. It forms small, opaque, white prisms, and if these are dissolved in tepid water, a salt is deposited, on cooling, which is decomposed by hot water into potassium hydrogen tartrate and tellurous anhydride.

The corresponding sodium salt, which crystallises with 2 mols. H_2O, is obtained in a similar manner. It separates from a concentrated solution in a bulky, white mass of rhombic crystals, which, if dried in the air and finally at 100°, are converted into small prisms. This salt is somewhat gelatinous, and it is very rapidly decomposed by boiling water into sodium hydrogen tartrate and yellowish tellurous anhydride.

Lithium telluryl tartrate is really a double compound of lithium tartrotellurite and lithium hydrogen tartrate. It has the composition $(C_4H_4O_6)_2Li_2TeO,(C_4H_4O_6LiH)_2 + 2H_2O$, and is obtained in a similar manner to the preceding compounds. It crystallises in a confused mass of orthorhombic needles, which are very difficult to purify.

Potassium telluryl citrate or *potassium citrotellurite*,

$$(C_6H_5O_7)_2K_2TeOH_2 + H_2O,$$

is obtained by adding the proper quantity of citric acid to a solution of potassium tellurite and evaporating the liquid carefully to dryness. It forms a white mass of small leaflets, very soluble in water, by which it is seemingly not decomposed.

Lithium telluryl citrate is gummy and non-crystallisable.

C. H. B.

Action of Ethyl Chlorolevulinate on Ethyl Sodomalonate. By M. Conrad and M. Guthzeit (*Ber.*, **19**, 42—45).—*Ethyl α-carboxyl-β-acetylglutaric acid*, $CH(COOEt)_2\cdot CHAc\cdot CH_2\cdot COOEt$, is obtained by

the action of ethyl chlorolevulinate on ethyl sodomalonate; it is an oil boiling at 285—295° (compare Abstr., 1885, 42). The free acid, $CH(COOH)_2{\cdot}CHAc{\cdot}CH_2{\cdot}COOH$, forms a crystalline mass, which softens at 100°, and melts at 121—124°. When heated to 160°, the acid loses carbonic anhydride and is converted into *β-acetylglutaric acid*, $CHAc(CH_2{\cdot}COOH)_2$. This is crystalline and melts at 109°. The barium and silver salts are described. A. J. G.

Combination of Acetamide with Metallic Chlorides. By G. André (*Compt. rend.*, **102**, 115—118).—The metallic chlorides were added gradually to a solution of acetamide in absolute alcohol, the liquid filtered, and the filtrate carefully evaporated in a vacuum. The addition of ether promotes the separation of the products.

Cupric chloride yields a compound of the composition $2NH_2Ac,CuCl_2$, which separates in soft green nodules. When heated in a current of hydrogen, it begins to lose acetamide at 100°, and at 150° melts to a black liquid which remains viscous when cooled, and is only partially soluble in water.

Cadmium chloride yields a similar compound which separates in small crystals.

Mercuric chloride forms a crystalline double compound, $NH_2Ac,HgCl_2$, which melts at 125° with slight volatilisation of acetamide, and decomposes at a higher temperature. In one experiment, a compound, $3NH_2Ac,HgCl_2$, was obtained, but subsequent attempts to prepare it gave negative results. Mercurous chloride shows little or no tendency to combine with acetamide.

Nickel chloride yields a green compound, $NiCl_2,4NH_2Ac+2H_2O$, and cobalt chloride forms a blue compound, $CoCl_2,4NH_2Ac + 2H_2O$, both of which crystallise with difficulty. The cobalt salt is very hygroscopic; it melts at about 62°, and if heated in a current of hydrogen for two hours at 110—115° it becomes anhydrous without losing more than traces of acetamide.

These compounds seem to be additive-products similar to those formed by ammonia. C. H. B.

Amyl Thiochlorocarbonate and its Action on Compounds containing Nitrogen. By H. Schöne (*J. pr. Chem.* [2], **32**, 241—261).—Amyl thiochlorocarbonate, $C_5H_{11}{\cdot}S{\cdot}COCl$, is prepared by saturating amyl mercaptan with carbonyl chloride and allowing the mixture to remain for some days. It is a highly refractive liquid of sp. gr. 1·078 at 17·5°, and boils without decomposition at 193°. When warmed with an equivalent quantity of sodium methoxide or sodium methosulphide, it yields methyl amyl thiocarbonate or dithiocarbonate. When dry ammonia is passed into cooled amyl thiochlorocarbonate, *amyl thiocarbamate*, $C_5H_{11}{\cdot}S{\cdot}CONH_2$, is formed; this crystallises in brilliant white plates, and melts at 107°; when warmed with alcoholic potash, amyl mercaptan, ammonia, and potassium carbonate are formed; with alcoholic ammonia, it yields carbamide and amyl mercaptan; strongly heated with aniline, it gives diphenylcarbamide; and it yields insoluble precipitates with silver nitrate, mercury chloride, and platinum chloride.

Amyl thiocarbanilate, $C_5H_{11}\cdot S\cdot CO\cdot NHPh$, is formed by the action of 1 mol. of amyl thiochlorocarbonate on 2 mols. of aniline. It crystallises in long needles which melt at 67°. It is decomposed by alcoholic potash into amyl mercaptan, aniline, and potassium carbonate, and by alcoholic ammonia into monophenylcarbamide and amylmercaptan.

Amyl thioallophanate, $C_5H_{11}\cdot S\cdot CO\cdot NH\cdot CO\cdot NH_2$, is formed by digesting together on a water-bath amyl thiochlorocarbonate and carbamide. It crystallises in needles and melts at 176°; it is easily decomposed by boiling water, alcoholic ammonia, and alcoholic potash. Heated in a sealed tube with acetic chloride, it yields *amyl thioacetylallophanate*, $C_5H_{11}\cdot S\cdot CO\cdot NH\cdot CO\cdot NHAc$; this crystallises in needles and melts at 85°.

Amyl dithiophenylallophanate, $C_5H_{11}\cdot S\cdot CO\cdot NH\cdot CS\cdot NHPh$, is formed by the action of monophenylthiocarbamide on amyl thiochlorocarbonate; it crystallises in large prismatic needles which melt at 102°; it forms an acetyl-derivative melting at 240°.

Amyl dithiodiphenylallophanate, $C_5H_{11}\cdot S\cdot CO\cdot NPh\cdot CS\cdot NHPh$, is formed by the action of diphenylthiocarbamide on amyl thiochlorocarbonate; it crystallises in very fine prismatic needles melting at 87°; it forms insoluble precipitates with silver nitrate, mercury, and platinum chloride. It does not form compounds with acetic chloride and benzoic chloride; when treated with an ammoniacal alcoholic solution of mercuric oxide, it yields *diphenylguanidine*,

$$NHPh\cdot C(NH)\cdot NHPh,$$

which melts at 147°. G. H. M.

Alkophyr and Biuret. By E. Brücke (*Chem. Centr.*, 1885, 905; comp. Abstr., 1871, 410, and 1883, 1019).—"Alkophyr" is the name given by the author to a hygroscopic substance which is isolated by a special process, described in this and former papers, from the peptones produced by the action of artificial gastric juice on blood-fibrin. Like biuret, it gives with cupric salts in presence of alkali, a red colour, which is changed to blue on passing carbonic anhydride. Yet biuret in the free state is not contained in the substance, whence the author supposes that a biuret residue is present in the molecule of "alkophyr." "Alkophyr" is a very stable compound; after it has been heated with hydrochloric, sulphuric, or nitric acid, or with baryta-water, the copper reaction can still be obtained.

W. R. D.

Compounds of the Uric Acid Series. By R. Behrend (*Annalen*, **231**, 248—256).—Bromomethyluracil is conveniently prepared by slowly dropping bromine into a flask containing carbon bisulphide and methyluracil. This compound is converted into amidomethyluracil by the action of ammonia at 150°. *Amidomethyluracil*, $NH_2\cdot C_5H_5N_2O_2 + H_2O$, crystallises in rhombic plates, soluble in alcohol and in water. The *hydrochloride*, $NH_2\cdot C_5H_5N_2O_2,HCl + H_2O$, forms monoclinic crystals, and the *platinochloride* crystallises in needles containing 2 mols. H_2O. *Methylhydroxyxanthine*, $C_6H_8N_4O_3 + 2H_2O$ is formed by the action of potassium cyanate on an aqueous solution of the

hydrochloride. It is sparingly soluble in cold water and insoluble in alcohol, but dissolves readily in solutions of the alkalis or alkaline carbonates. It also dissolves in strong sulphuric acid, but is reprecipitated on dilution with water. Acetic anhydride at 160° converts the compound into the acetic derivative of amidomethyluracil which crystallises in rhombic prisms.

Trimethyluracil, $C_5H_4N_2O_2Me_2$, is obtained by the action of methyl iodide on the potassium salt of methyluracil at 150°. The crude product is evaporated with a small portion of sodium carbonate and extracted with chloroform. The chloroform solution is evaporated and the residue treated with alcohol, which leaves dihydromethyluracil undissolved. Pure trimethyluracil melts at 103—104°. It is freely soluble in water, alcohol, chloroform, and methyl iodide.

W. C. W.

Tetrachlorothiophen Tetrachloride. By C. Willgerodt (*J. pr. Chem.* [2], **33**, 150—151).—This compound, C_4SCl_8, is formed when chlorine is passed through a solution of moniodothiophen in chloroform. The iodine liberated in the reaction is removed by means of soda; the chloroform is then evaporated and the residue washed with alcohol and crystallised from chloroform. It forms large, thick prisms melting at 215°, very readily soluble in chloroform, ether, benzene, carbon bisulphide, &c. It has a sharp penetrating odour.

N. H. M.

Thiophendisulphonic Acid. By H. Jaekel (*Ber.*, **19**, 184—196).—*Potassium thiophendisulphonate*, $C_4SH_2(SO_3K)_2 + H_2O$, is prepared by treating lead thiophensulphonate (80 grams) with fuming sulphuric acid (100 grams), and pouring the mixture into water, when it becomes viscid and evolves sulphurous anhydride. The solution so obtained is saturated with lead carbonate, filtered, evaporated, and treated with potassium carbonate. The mixed salts of the mono- and di-sulphonic acids so obtained were separated by fractional crystallisation, the disulphonate crystallising first. The sodium and barium salts, each crystallising with 3 mols. H_2O, were also prepared. The *free acid* was prepared by decomposing the pure lead salt with hydrogen sulphide; it is an indistinctly crystalline mass, readily soluble in water and alcohol, and has an intensely sour taste and acid reaction. The *chloride*, $C_4SH_2(SO_2Cl)_2$, prepared by the action of phosphoric chloride on the potassium salt, crystallises in groups of silky white needles, and melts at 77—77·5°. The chloride of the isomeric acid prepared by Langer (Abstr., 1885, 765) melts at 148—149°. The *amide*, $C_4SH_2(SO_2NH_2)_2$, crystallises in flat prisms and melts at 211·5°.

Dicyanothiophen, $C_4SH_2(CN)_2$, is obtained by heating, in small quantities, a mixture of equal parts of anhydrous potassium thiophendisulphonate and potassium cyanide. It forms small, white, odourless crystals, and melts at 92—92·5°. When boiled with alcoholic potash, &c., it yields a thiophendicarboxylic acid identical with that obtained by Messinger (Abstr., 1885, 767) by the oxidation of thioxylen. The silver, barium, and calcium salts of this acid are described. The *chloride* crystallising in needles and the amide were obtained, but in quantity too small for proper examination.

A. J. G.

Iron Compounds as Carriers of Bromine. By A. Scheufelen (*Annalen*, **231**, 152—195).—Anhydrous ferrous bromide is most readily prepared by passing a current of carbonic anhydride and bromine through a hot porcelain tube containing metallic iron. The bromide sublimes, forming greenish-yellow scales which deliquesce on exposure to the air. Ferric bromide is obtained by bringing a mixture of ferrous bromide (1 part) and dry bromine (2 parts) into a strong glass tube. After removing the air, the tube is sealed at the blowpipe and heated at 170—200° for six hours. Ferric chloride crystallises in rhombic six-sided plates, exhibiting a metallic lustre. It is very hygroscopic and dissolves freely in alcohol, ether, and water. Ferric bromide cannot be sublimed as it is decomposed by heat. When it is heated in a glass tube from which the air has been exhausted, it dissociates into ferrous bromide and bromine. On cooling, ferric bromide is again produced.

By the action of bromine and ferric bromide on nitrobenzene in sealed tubes at 110°, metabromonitrobenzene together with a little tetrabromaniline is produced and hydrogen bromide is liberated. If the tubes are kept at 120° for 30 hours, no hydrogen bromide escapes when they are opened, and the yield of tetrabromaniline is largely increased. The production of tetrabromaniline is minimised by working at a temperature of 80° and opening the tubes from time to time to permit the hydrgen bromide to escape.

In these experiments, the ferric bromide may with advantage be replaced by a mixture of bromine and ferrous bromide or bromine and ferric chloride. In the latter case, the whole of the chlorine escapes as hydrogen chloride. It is essential that the ferric chloride should be absolutely free from moisture.

Paradibromonitrobenzene can be easily prepared by the action of bromine and ferrous bromide on nitrobenzene in sealed tubes. The mixture is heated at 60° for some time, the tubes are opened to allow the hydrogen bromide to escape; they are then resealed and heated at 80°.

Action of Bromine on the Isomeric Nitrotoluenes in the presence of Ferrous and Ferric Bromide.—When anhydrous ferrous bromide is used substitution takes place in the benzene nucleus, but in the presence of moisture the side chain is also attacked. Paranitrotoluene and anhydrous ferrous bromide yield either orthobromoparanitrotoluene, melting at 77·5°, or a mixture of orthodibromoparanitrotoluene, melting at 58°, and tetrabromotoluidine, melting at 226°, according to the relative quantity of bromine used in the preparation. These compounds have been described by Neville and Winther (Trans., 1880, 429, and 1881, 84).

If the ferrous bromide used in this experiment is allowed to deliquesce by exposure to the air, paranitrobenzyl bromide is produced. This compound, which melts at 100°, has been previously described by Wackendorff (this Journal, 1877, i, 207).

On brominating metanitrotoluene in the presence of ferrous bromide, a mixture of orthobromometanitrotoluene and parabromometanitrotoluene is obtained. The former product melts at 78° and the latter

at 31°. They have both been previously described by Neville and Winther (*loc. cit.*).

Monobromonitronaphthalene is formed by the action of bromine and ferric bromide on nitronaphthalene.

A mixture of paradibromobenzene, melting at 89°, unsymmetrical tribromobenzene, and symmetrical tetrabromobenzene is produced by the action of bromine ($3\frac{1}{2}$ mols.) on benzene and ferric chloride contained in a flask provided with a reflux condenser. By using a larger proportion of bromine, perbromobenzene, C_6Br_6, can be prepared.

W. C. W.

Ferric Chloride as a Carrier of Iodine. By L. Meyer (*Annalen*, **231**, 195—196).—Moniodobenzene is formed by heating benzene, ferric chloride, and iodine in a sealed tube. This reaction will probably provide an easy method of preparing iodine substitution products.

W. C. W.

Crystallographical Investigations. By K. Haushofer (*Zeit. Kryst. Min.*, **11**, 147—157).—The author gives the results of measurements of crystals of the following compounds:—α-Metadiquinoline, $C_{18}H_{12}N_2$, melting at 159°, monosymmetric, $a:b:c = 2{\cdot}3226:1:1{\cdot}0916$; $\beta = 74°\ 55'$. α-Metadiquinoline, melting at 115°, isomeric with the preceding, asymmetric, $a:b:c = 1{\cdot}8129:1:1{\cdot}4823$; $\alpha = 88°\ 34'$, $\beta = 106°\ 19'$, $\gamma = 89°\ 12'$. 2′ : 3′ Methylquinolinecarboxylic acid, $C_{11}H_9NO_2$, monosymmetric, $a:b:c = 1{\cdot}3514:1:0{\cdot}6128$; $\beta = 86°\ 16'$. 2′ : 3 Propylethylquinoline nitrate, monosymmetric, $a:b:c = 1{\cdot}8813:1:1{\cdot}4685$; $\beta = 75°\ 40'$. 2′ : 3′ Propylethylquinoline hydrochloride, $C_{14}NH_{17},HCl + 2H_2O$, asymmetric, axial ratios not given. Chloropropylcinnamic acid, CPhCl : CPr·COOH, asymmetric, $a:b:c = 1{\cdot}2551:1:1{\cdot}1661$; $\alpha = 122°\ 33'$, $\beta = 106°\ 21'$, $\gamma = 69°\ 25'$. Ethyl paranitrobenzoylacetate, monosymmetric,

$$a:b:c = 0{\cdot}3584:1:2380;$$

$\beta = 72°\ 22'$. Methyl paranitrobenzoylacetate, monosymmetric, $a:b:c = 0{\cdot}4933:1:?$; $\beta = 56°\ 5'$. Ethyl paranitrobenzoyltetramethylenecarboxylate, monosymmetric, $a:b:c = 2{\cdot}3530:1:1{\cdot}8530$; $\beta = 80°\ 42'$. Trimethylenedicarboxylic acid, asymmetric, $a:b:c = 0{\cdot}7712:1:0{\cdot}8702$; $\alpha = 88°\ 41'$, $\beta = 92°\ 40'$, $\gamma = 92°\ 38'$. Ethyl diphenylfurfuranedicarboxylate, rhombic, $a:b:c = 0{\cdot}9005:1:0{\cdot}6309$. Metaxylylene dibromide, $C_6H_4(CH_2Br)_2$, monosymmetric, $a:b:c = 2{\cdot}6562:1:3{\cdot}1130$; $\beta = 86°\ 26'$. Ethyl oxyhexamethylenedicarboxylate, asymmetric, $a:b:c = 0{\cdot}7741:1:0{\cdot}3371$; $\alpha = 89°\ 40'$, $\beta = 98°\ 18'$, $\gamma = 89°\ 50'$. Diallylmalonic acid, rhombic, $a:b:c = 0{\cdot}9916:1:1{\cdot}0179$. Ethyl malonparatoluidate,

$$C_6H_4Me{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}COOEt,$$

rhombic, $a:b:c = 0{\cdot}9320:1:2$.

A. J. G.

Aromatic Iodochlorides. By C. Willgerodt (*J. pr. Chem.* [2], **33**, 154—160).—*Phenyl iodochloride*, $PhICl_2$, is prepared by passing chlorine into a solution of 5 grams of iodobenzene in 10—12 grams of chloroform. In a short time the whole solidifies to a crystalline mass

which is then dried between filter-paper. It crystallises from chloroform in yellow needles, soluble in warm benzene and glacial acetic acid, sparingly soluble in boiling light petroleum, carbon bisulphide, and ether. When heated at 115—120°, it gives up chlorine, but not hydrogen chloride, leaving iodobenzene. The same change takes place when the substance is kept over sulphuric acid; on the other hand, it may be kept for months exposed to air without decomposition. When digested slowly with alcohol, iodobenzene and aldehyde are formed. Owing to the readiness with which it decomposes metallic and alkyl iodides, phenyl iodochloride may be used as a test for iodine. It reacts with aniline and quinoline with formation of chlorine-derivatives.

Parabromophenyl iodochloride, $C_6H_4BrICl_2$, crystallises in yellow needles, readily soluble in ether, chloroform, and benzene. It melts at 119—120° with violent effervescence.

Symmetrical α-tribromophenyl iodochloride, $C_6H_2Br_3ICl_2$, resembles in its behaviour the monobromo-derivative. It is readily soluble in carbon bisulphide, ether, benzene, &c.

Paranitrophenyl iodochloride, $NO_2{\cdot}C_6H_4ICl_2$, forms short, thick, yellow prisms, soluble in chloroform and benzene. When heated at 150°, it gives up chlorine, leaving pure paranitroiodobenzene.

N. H. M.

Phenyl Isocyanate. By F. Gumpert (*J. pr. Chem.* [2], **32**, 278—300).—Primary and secondary alcohols combine directly with phenyl isocyanate, forming urethanes. With isopropyl alcohol, phenyl isocyanate forms *isopropyl phenylcarbamate*, $NHPh{\cdot}COOPr^{\beta}$, which crystallises in white needles, and melts at 90° without decomposition. With *benzoïn* it forms a crystalline compound, *carbanilidobenzoïn*, $NHPh{\cdot}CO{\cdot}CPh(OH){\cdot}COPh$, melting at 163°. Phenol also combines with phenyl isocyanate, forming *phenyl phenylcarbamate*,

$$NHPh{\cdot}COOPh,$$

which yields sodium carbonate, aniline, and phenol when treated with soda, showing that it is a true urethane; when treated with dilute aqueous ammonia, phenyl phenylcarbamate yields monophenylcarbamide. When phenyl isocyanate is heated with orthonitrophenol in sealed tubes at 150—170° for some hours, a slight reaction takes place, and a small quantity of *nitrophenyl phenylcarbamate*,

$$NHPh{\cdot}COOC_6H_4{\cdot}NO_2,$$

is formed; it crystallises in white needles, and melts at 115°.

The author uses the reaction of phenyl isocyanate with alcohols to determine the constitution of *isatin*, which may be regarded as *azobenzoyl carbinol*. Equal molecules of isatin and phenyl isocyanate combine according to the equation $C_8H_5NO_3 + C_6H_5CON = C_{15}H_{10}N_2O_3$; the compound thus obtained, *carbanilidoisatin*,

$$CO<\begin{matrix}-CO-\\C_6H_4\end{matrix}>N{\cdot}CO{\cdot}NHPh,$$

forms yellow crystals, melting with decomposition at 180—185°.

When *carbanilidoisatin* is dissolved in sulphuric acid, and benzene

added, an intense blue colour is produced and *indophenin* is formed. With dilute alkalis, it forms the salts of *carbanilidoisatinic acid*, $NHPh{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CO{\cdot}COOH$; the free acid is crystalline, and melts at 175°; with alcoholic ammonia, the amide of the above acid is formed; it melts at 229°; with ethylamine, phenylhydrazine, and hydroxylamine, additive compounds are also formed. When phenyl isocyanate acts on *anthranilic acid*, 1 : 2 *amidobenzoyldiphenylcarbamide* is formed by direct combination of 2 mols. of the isocyanate with 1 mol. of anthranilic acid; with acetic anhydride, it forms *diacetanilide*, $C_6H_5{\cdot}NAc_2$, which yields *acetanilide* on distillation. Chlorine combines with phenyl isocyanate, forming phenyl isocyanate dichloride, $C_6H_5{\cdot}CON{\cdot}Cl_2$; this is decomposed by water, forming *carbanilide*, and apparently gives *monochlorophenyl isocyanate*, with the loss of hydrogen chloride, on evaporation of a solution in chloroform. Bromine behaves in the same way. By the successive action of phosphorus pentachloride and zinc-dust, phenyl isocyanate is converted into methylaniline.

G. H. M.

Chlorinated Ethylbenzenes. By Istrati (*Ann. Chim. Phys.* [6], **6**, 475—505).—In continuation of his researches (this vol., p. 230), the author has prepared the following chlorinated ethylbenzenes, by passing ethylene into a mixture of the corresponding chlorobenzene and aluminium chloride, the different members of the series being separated by fractional distillation. They are compounds having an aromatic odour, and, with two exceptions, are liquids at 7°. They are all readily soluble in the usual solvents, with the exception of alcohol and benzene, in which they dissolve somewhat less easily. The author remarks that these compounds become more difficult to oxidise with increase in the amount of chlorine.

Paradichlorethylbenzene, $C_6H_3EtCl_2$ [$Et : Cl_2 = 1 : 3 : 6$], prepared from paradichlorobenzene, boils at 213·5°, its sp. gr. = 1·239 at 0°; by oxidation with chromic mixture, *dichlorobenzoic acid*, $C_6H_3Cl_2{\cdot}COOH$ [$COOH : Cl_2 = 1 : 3 : 6$], is formed, and is identical with Beilstein and Kuhlberg's β-dichlorobenzoic acid; the author however finds the copper salt to be quite white when first precipitated, and only to become blue after a time; it is slightly soluble in alcohol. The *ammonium*, *potassium*, and *iron* salts were also prepared.

Paradichlorodiethylbenzene, $C_6H_2Et_2Cl_2$, boils at about 248—250°; its sp. gr. = 1·179 at 0°.

Paradichlorotriethylbenzene, $C_6HEt_3Cl_2$, boils at 268—276°, it becomes yellow by exposure to the air; its sp. gr. = 1·131 at 0°; a mononitro-substitution compound, $C_6Et_3Cl_2{\cdot}NO_2$, is formed by boiling it with excess of strong nitric acid; it melts at 20°, is of a yellowish colour, and distils with partial decomposition between 310° and 315°. A sulphonic acid, $C_6Et_3Cl_2{\cdot}SO_3H$, was prepared in small amounts by boiling with concentrated sulphuric acid for 20 minutes.

Paradichlorotetrethylbenzene, $C_6Et_4Cl_2$, is a viscous, oily liquid; its sp. gr. = 1·129 at 0°; it boils between 293° and 299°.

Trichlorethylbenzene, $C_6H_2EtCl_3$, prepared from 1 . 2 . 4 trichlorobenzene, is a mobile liquid; it boils at 243—252°, and its sp. gr. = 1·389 at 0°.

Trichlordiethylbenzene, $C_6HEt_2Cl_3$, is an oily liquid, which gradually

becomes coloured yellow on keeping; its sp. gr. = 1·305 at 0°, and it boils at 268—273°.

Trichlorotriethylbenzene, $C_6Et_3Cl_3$ [$Et_3 = 3 : 5 : 6$], is an oily liquid; it boils at 295—300°; its sp. gr. = 1·240 at 0°.

The tetrachlorethylbenzenes were prepared with some difficulty from 1 . 3 . 4 . 5 tetrachlorobenzene, this chlorobenzene being so volatile that the operation had to be conducted at a low temperature, only just above the melting point; this difficulty is increased when the more volatile 1 . 2 . 4 . 5 tetrachlorobenzene is employed; small quantities of its two ethyl-derivatives were, however, obtained; they are solids at the ordinary temperature. 1 . 3 . 4 . 5 *Tetrachlorethylbenzene*, C_6HEtCl_4, boils at 270—275°; it is of a pale-yellow colour, and its sp. gr. = 1·543 at 0°, and from this *mononitrotetrachlorethylbenzene*,

$$C_6EtCl_4{\cdot}NO_2 \ [NO_2 : Et = 2 : 6],$$

was prepared; it melts at 28—30°, and remains in a state of superfusion at 21°; by treatment with aluminium chloride and ethylene, it appears to be partially converted into tetrachlorodiethylbenzene.

1 . 3 . 4 . 5 *Tetrachlorodiethylbenzene*, $C_6Et_2Cl_4$ [$Et_2 = 2 : 6$], is a solid which crystallises in prisms; it melts at 45° and boils at 290°; its sp. gr. = 1·431 at 15°.

Pentachlorethylbenzene, C_6EtCl_5, prepared from pentachlorobenzene, is a white, crystalline substance; it melts at 85° and boils at about 300°; its sp. gr. = 1·7205 at 19°; by oxidation with potassium permanganate, it yields what is probably pentachlorobenzoic acid; it is however very unstable, being decomposed by alkalis into pentachlorobenzene and carbonic anhydride. A. P.

Nitration of Benzyl Chloride. By E. Nölting (*Ber.*, **19**, 137).—The author points out that, unknown to him, Abelli had proved the presence of orthonitrobenzyl chloride (Abstr., 1883, 1092) in the oil formed during the nitration of benzyl chloride, before the author's note on that subject (Abstr., 1884, 1005) was published. L. T. T.

Nitro-derivatives of Paraxylene. By E. Nölting and C. Geissmann (*Ber.*, **19**, 144—145).—Lellmann has recently (Abstr., 1885, 973) proved the constitution of the three dinitroparaxylenes. The diamine from the dinitro-xylene melting at 94°, forms silky needles melting at 75°. The hydrochloride is coloured deep-red by ferric chloride, but even on heating no quinone is formed. With sodium nitrite in hydrochloric acid solution, a substance having the characteristics of an azimido-derivative is formed, showing the base to be an orthodiamine. The diamine from the nitro-derivative, melting at 124°, forms white, silky needles melting at 101·5—102·5°. The hydrochloride forms with sodium nitrite a brown dye-stuff, with diazo-compounds a chrysoïdine colouring matter, and with nitrosodimethylaniline a compound analogous to Witt's toluylene-blue. It is therefore a meta-compound. These results confirm Lellmann's conclusions. *Trinitroparaxylene*, obtained by heating paraxylene with fuming nitric acid and sulphuric acid, forms crysta s melting at 139—140°. When subjected to continued boiling with alcoholic ammonia, *dinitroparaxylidine*, [$Me_2 : NO_2 : NO_2 : NH_2 =$

1 : 4 : 3 : 5 : 2], is obtained crystallising in needles melting at 202—203°. When the NH_2 group is eliminated by means of the diazo-reaction, metadinitro-xylene is formed. L. T. T.

Preparation of Mononitroanisoïls and Mononitrophenetoïls by Kolbe's Method. By C. Wilgerodt and M. Ferko (*J. pr. Chem.* [2], **33**, 152—153).—The alkali salts of mononitrophenols are heated with an excess of alkaline ethyl sulphate in presence of alcohol at a temperature not exceeding 200°. The product is treated with water and steam distilled. In this way paranitranisoïl and paranitrophenetoïl were obtained very pure; the former compound melts at 54°, and the latter at 60°. The ortho-compounds were obtained as oils. Paranitrophenetoïl is only slightly decomposed by water at 150°. N. H. M.

Symmetrical Diphenyl Glyceryl Ether. By A. Rössing (*Ber.*, **19**, 63—68).—*Symmetrical diphenyl glyceryl ether*, $OH{\cdot}CH(CH_2{\cdot}OPh_2)$, is prepared by the action of symmetrical dichlorhydrin on potassium phenoxide; it crystallises in nacreous plates, melts at 80—81°, can be sublimed, is very readily soluble in ether, benzene, chloroform, and hot alcohol, sparingly soluble in cold alcohol, and insoluble in water. Aqueous potash decomposes it into phenol and glycerol. The sodium-derivative, $ONa{\cdot}CH(CH_2{\cdot}OPh)_2$, is obtained by the action of sodium on a solution of the ether in benzene, as an indistinctly crystalline mass. The *acetate*, $COMe{\cdot}O{\cdot}CH(CH_2{\cdot}OPh)_2$, obtained by the action of the equivalent quantity of acetic chloride on the ether, is crystalline, melts at 70—71°, and is insoluble in water, but readily soluble in benzene, chloroform, ether, and alcohol. If excess of acetic chloride is employed, and the mixture heated for 1½ to 2 hours, a *triacetyl*-derivative, $C_{21}H_{22}O_6$, is obtained as a yellow oil. The *benzoate* melting at 66—67° and the *tribenzoyl* compound were prepared in a similar manner.

The *metadisulphonic acid*, $OH{\cdot}CH(CH_2{\cdot}O{\cdot}C_6H_4{\cdot}SO_3H)_2$, prepared by dissolving the ether in concentrated sulphuric acid with the aid of heat, was only obtained in moderately concentrated solution. The potassium salt, $C_{15}H_{14}O_9S_2K_2 + 2H_2O$, and the barium salt were prepared. The ethyl salt could not be prepared. When the potassium salt is heated with strong aqueous potash in sealed tubes at 140—150°, resorcinol, glycerol, and potassium sulphite are formed. A. J. G.

Trinitrometacresol. By E. Nölting (*Ber.*, **19**, 136).—This substance may readily be obtained by diazotizing metatoluidine, and heating the product with nitric acid. It has already been obtained from metacresol (Abstr., 1883, 59). It is thus seen that the toluidines and cresols behave similarly with nitric acid, the ortho- and para-compounds yielding di-, the meta tri-nitro-derivatives. L. T. T.

Properties of 1 : 3 : 4 Metaxylenol. By O. Jacobsen (*Ber.*, **18**, 3463—3464).—Staedel and Hölz have recently described 1 : 3 : 4 metaxylenol as a crystalline mass melting at 27—29° and boiling at 216·5° (this vol., p. 145), whilst the author had prepared it from several sources, but had always obtained it as a liquid not solidifying at − 20°

and boiling at 211·5°. It is now shown that this substance exhibits the property of surfusion in a high degree; it can be solidified by about three days' exposure to a cold of − 4°, but crystallises at once on addition of a particle of the already solidified substance. Experiments with large quantities of the substance show that the melting point is 25·4—26°. Staedel has repeated his determination of the boiling point of the substance and finds it to be 211·5°, that given by the author. A. J. G.

Carvacrol and its Derivatives. By S. Lustig (*Ber.*, **19**, 11—18).—The sodium-derivative of carvacrol is prepared by the action of sodium on a solution of carvacrol in light petroleum; it is a white crystalline powder.

Ethylcarvacrol, $C_{10}H_{13}EtO$, is obtained by the action of ethyl iodide on the sodium-derivative; it is an oily liquid of carrot-like odour, boils at 235°, and is lighter than water. *Benzoylcarvacrol*, $C_{10}H_{13}BzO$, prepared by the action of benzoic chloride on carvacrol, is a viscid, yellowish-green oil, boils at 260°, and is heavier than water. *Acetylcarvacrol*, prepared in a similar manner, is a colourless liquid heavier than water.

Paracarvacrotic aldehyde, $OH{\cdot}C_{13}H_{12}{\cdot}COH$, is prepared by the action of chloroform and concentrated aqueous soda on carvacrol, the liquid being then acidified and distilled with steam, when the aldehyde passes over. It is a clear yellow oil, heavier than water, and cannot be distilled alone without decomposition. It gives a mirror when heated with an ammoniacal silver solution; with ferric chloride in alcoholic solution, it gives a dark-green coloration. Like other aromatic aldehydes, it does not give a crystalline compound with sodium hydrogen sulphite. When exposed to air, it is oxidised to the corresponding acid. The author has also obtained the crystalline substance which Nordmann obtained by this reaction and described as paracarvacrotic aldehyde (Abstr., 1885, 162), he suggests that it is possibly a polymeric modification.

Paracarvacrotic acid, $OH{\cdot}C_{10}H_{12}{\cdot}COOH$, is prepared by the oxidation of the aldehyde either by exposure to air or by treatment with potassium permanganate, or by boiling the aldehyde with alcoholic potash. It crystallises in long, white, silky, very slender needles, melts at 80°, is nearly insoluble in cold water, readily soluble in hot water, alcohol, and ether. It can be sublimed, and distils with steam. It gives a green coloration with ferric chloride. This acid is isomeric with that obtained by Kekulé and Fleischer (this Journ., 1874, 66), by the action of sodium and carbonic anhydride on carvacrol. It is probable that in the latter acid the hydroxyl and carboxyl groups are in the ortho-position relatively to one another, whilst in the author's acid they are in the para-position. A. J. G.

Identity of Isorcinol and Cresorcinol. By E. Nölting and Weingaertner (*Ber.*, **19**, 136—137).—Hitherto the m. p. of isorcinol, obtained by melting toluenedisulphonic acid [$Me : SO_3H : SO_3H = 1 : 2 : 4$] with potash (this Journal, 1873, 505), has been given as 95° when hydrated, 87—88° when anhydrous. By treating the aqueous

solution of crude isorcinol with calcium carbonate, filtering off the precipitated salicylate, extracting the isorcinol from the filtrate with ether, evaporating the ether and extracting the solid residue with chloroform, the authors obtained isorcinol in small needles melting at 102—104°, and having all the properties of cresorcinol (Winter and Wallach give 104—105° as m. p. of the latter). The two substances are therefore identical. The best mode of preparation is from amido-orthocresol [Me : OH : NH_2 = 1 : 2 : 4]. L. T. T.

Metanitrodimethylaniline, Metanitrodiethylaniline, and their Reduction-products. By A. Groll (*Ber.*, **19**, 198—201).—Nölting and Collin have stated that dimethylaniline when nitrated yields paranitrodimethylaniline, free from its isomerides; on repeating their experiments, however, it was found that the metanitro-compound was always the main product. *Metanitrodimethylaniline* crystallises in large, compact, red prisms, melts at 60—61°, and distils with partial decomposition at 280—285°; its basic powers are less marked than those of the para-compound. When reduced, it yields *dimethylmetaphenylenediamine;* this is an oil boiling at 268—276° under a pressure of 740 mm., not solidifying at − 15°, and of sp. gr. 0·995 at 25°; the hydrochloride and sulphate crystallise well; the base reacts with nitrous acid to form a dye closely resembling Bismark-brown in shade, and with diazobenzene chloride to form dimethyl-chrysoïdine chloride crystallising in needles.

Metanitrodiethylaniline is a deep-yellow oil boiling at 288—290°.

Diethylmetaphenylendiamine is a pale-yellow oil boiling at 276—278°, and giving similar reactions to the methyl compound.

A. J. G.

Hydrogen Sulphates of Aromatic Amines. By C. Wellington and B. Tollens (*Ber.*, **18**, 3311—3314).—*Hydrogen paratoluidine sulphate* is obtained as a crystalline substance by dissolving toluidine (1 mol.) in sulphuric acid (3½ mols.). *Hydrogen orthotoluidine sulphate* is prepared by the action of a cooled mixture of 10½ times the theoretical amount of sulphuric acid with an equal weight of water on orthotoluidine. *Hydrogen aniline sulphate* is obtained by the action of 4·6 times the theoretical amount of sulphuric acid on aniline; the product is filtered as quickly as possible, and washed with absolute alcohol and then with ether. It crystallises in plates. It is very unstable, decomposing in presence of moisture into normal aniline sulphate and free sulphuric acid. N. H. M.

Ethylparaphenylenediamine. By W. Schweitzer (*Ber.*, **19**, 149—150).—This compound, $NH_2 \cdot C_6H_4 \cdot NHEt$, is prepared by reducing nitrethylaniline with tin and hydrochloric acid, decomposing the stannochloride formed, with potash, and extracting with ether. It is a clear yellow, odourless oil, which soon becomes brown-coloured and viscid. It boils at 261—262° under 746 mm. pressure, is readily soluble in benzene, alcohol, and ether, less soluble in water and dilute aqueous potash. When fused with phenol, or α- or β-naphthol, it yields colouring matters of the indophenol class.

Paranitrethylaniline is most conveniently prepared by heating a mixture of 14 grams of paranitraniline, 11 grams of ethyl bromide, and 6 grams of potash dissolved in alcohol in a sealed tube for 3 to 4 hours at 100—110°. A. J. G.

Safranine. By W. Schweitzer (*Ber.*, **19**, 150—153).—Two isomeric monethylsafranines can be obtained. *α-Ethylsafranine*, $C_{18}H_{13}EtN_4$, is prepared by dissolving 10·4 grams of ethylparaphenylenediamine and 12·7 grams of aniline, both in the form of their hydrochlorides, in 700 c.c. of water, adding acetic acid, heating to boiling, and gradually adding 400 c.c. of a solution of potassium dichromate (40 grams per litre): milk of lime is now added and the red safranine solution filtered, evaporated to dryness, and the colouring matter extracted with absolute alcohol. The *hydrochloride* thus obtained is a very hygroscopic, bluish-green, crystalline powder of metallic lustre, insoluble in ether, readily soluble in water and alcohol to liquids ruby-red by transmitted, olive-green by reflected light. The *platinochloride*, $(C_{18}H_{13}EtN_4)_2,H_2PtCl_6$, crystallises in small, dark needles. The *free base*, prepared by the action of silver oxide on the hydrochloride, forms a non-crystalline mass of cantharidine-green colour by reflected light, but showing a ruby-red colour in thin layers by transmitted light. When the hydrochloride is treated with tin and hydrochloric acid, it is converted into the colourless leuco-compound; but neither the leuco-base nor its hydrochloride could be isolated.

β-Ethylsafranine is prepared by adding 20·4 grams of potassium dichromate dissolved in 340 c.c. of water to a hot solution of 10·8 grams of paraphenylenediamine, 7·7 grams of aniline, and 12·3 grams of ethylaniline in 500 c.c. of water, acetic acid being previously added. The hydrochloride so obtained is an amorphous mass of cantharidine lustre; it closely resembles the *α*-compound. The platinochloride forms a dark-violet crystalline powder. The free base and the leuco-compound also closely resemble the corresponding *α*-compounds. *α*-Ethylsafranine has greater tinctorial powers than its isomeride. A. J. G.

Azo-derivatives of Metaxylenol. By E. Grevingk (*Ber.*, **19**, 148).—*Phenylazometaxylenol*, $PhN_2{\cdot}C_6H_2Me_2{\cdot}OH$ [OH : N, = 1 : 2], is prepared by the addition of diazobenzene chloride to an alcoholic solution of metaxylenol; it crystallises in hair-like, brownish-red needles, of violet lustre, and melts at 175°. It is insoluble in water, readily soluble in alcohol, ether, light petroleum, benzene, and chloroform. When reduced, it yields aniline and orthamido-xylenol.

Diazobenzenesulphonic acid reacts in similar manner with an alcoholic solution of metaxylenol to form a sulphonic acid which dyes silk and wool brownish-red, and yields sulphanilic acid and orthamidoxylenol on reduction. Its sodium salt is obtained as a yellowish-brown flocculent precipitate; the barium salt,

$$(OH{\cdot}C_6H_2Me_2{\cdot}N_2{\cdot}C_6H_4{\cdot}SO_3)_2Ba,$$

is nearly insoluble in water. A. J. G.

Substance contained in Commercial Phenylhydrazine. By E. v. MEYER (*J. pr. Chem.* [2], **32**, 430).—This is a preliminary notice of a substance which has been found in commercial phenylhydrazine. It forms small plates, contains sulphur, melts at 96°, and is very unstable. The author is engaged in conjunction with Pfitzinger in the investigation of its composition. G. H. M.

Desulphurisation of Thiocarbamides by Mercuric Cyanide. By R. HEFELMANN (*Chem. Centr.*, 1885, 884—885).—This research was undertaken in order to ascertain to what extent Laubenheimer's methods for the desulphurisation of thiocarbamides by mercuric cyanide are generally applicable. Sulphocarbanilide, when treated with mercuric cyanide in presence of ammonia, yields, not phenylguanidine, but the hydrocyanocarbodiphenylimide described by Laubenheimer. Hydrocyanocarbodiphenylimide, when treated with acetic anhydride or chloride, yields an acetyl-derivative, $C_{14}H_{10}AcN_3$, which melts at 119—120°; with benzoic chloride, a benzoyl-derivative melting at 159° is obtained. When treated with excess of bromine in a cold glacial acetic acid solution, a dibromo-derivative,

$$C_6H_4Br\cdot N : C(CN)\cdot NH\cdot C_6H_4Br,$$

is obtained, which crystallises in yellowish-white, slender, prismatic needles melting at 178°. Diparatolylthiocarbamide, when desulphurised with mercuric cyanide, yields hydrocyanocarbodiparatolylimide, $C_6H_4Me\cdot N : C(CN)\cdot NH\cdot C_6H_4Me$, which forms greenish-white crystals melting at 124°; its monacetyl-derivative melts at 99—100°. In the same way, diorthotolylthiocarbamide yields hydrocyanocarbodiorthotolylimide, which melts at 105·6°, and like the corresponding para-compound is dimorphous; its acetyl-derivative melts at 131°. Hydrocyanocarbo-β-dinaphthylimide,

$$C_{10}H_7\cdot N : C(CN)\cdot NH\cdot C_{10}H_7,$$

melts at 106°; its acetyl-derivative melts at 141°; the benzoyl-derivative forms yellow, prismatic crystals melting at 187—188°. The dipseudocumidyl-compound could not be obtained quite free from sulphur and mercury; its melting point varied between 130° and 140°, whilst the acetyl compound melts at 131—132°. H. P. W.

Meta- and Para-phenylene Diphenyl Ketones (Iso, and Tere-phthalophenones). By E. NÖLTING and O. KOHN (*Ber.*, **19**, 146—147).—Recent researches (Abstr., 1884, 1024, 1187) have rendered it probable that phthalophenone and phthalic chloride have unsymmetrical formulæ. It seemed, however, likely that the formulæ of the phenones and chlorides of iso- and tere-phthalic acids are symmetrical. Isophthalophenone (metaphenylene diphenyl ketone) yields with hydroxylamine a *monoxime*, which forms crystals melting at 201°. *Paraphenylene diphenyl ketone* (*terephthalophenone*)—from terephthalic chloride, benzene, and aluminic chloride—forms small white scales melting at 156—157°, and very sparingly soluble in alcohol. With hydroxylamine, it yields a *monoxime*, forming crystals melting at 212—213°. From neither compound could a dioxime be obtained.

These results confirm the view of the symmetrical structure of these two compounds.

The authors believe that acids containing two carboxyl-groups attached to neighbouring carbon-atoms all form unsymmetrical chlorides (compare also Hjelt, Abstr., 1884, 297). L. T. T.

The Hydroxylamine Reaction. By F. Münchmeyer (*Ber.*, **19**, 153—155).—It has been assumed that only those diketones which contain two CO-groups united directly with one another react with 2 mols. of hydroxylamine to form dioximes. Paal has already brought forward one exception to the rule, by showing that acetonylacetone, $COMe\cdot CH_2\cdot CH_2\cdot COMe$, yields a dioxime, and the author now shows that dibutyryl, $Pr^{\alpha}\cdot CO\cdot COPr^{\alpha}$, gives a *monoxime* only; whilst by boiling terephthalophenone, $C_6H_4(COPh)_2$, for 10 hours with an alcoholic solution of free hydroxylamine, a *dioxime*, $C_6H_4(CPh:NOH)_2$, is obtained. The last result is not in accordance with a recent statement of Nölting and Kohn (preceding Abstract). A. J. G.

Trioxime of Phloroglucinol. By A. Baeyer (*Ber.*, **19**, 159—163; compare this vol., p. 223).—This substance is prepared by dissolving 1 part of crystalline phloroglucinol in 45 parts of water, adding 1·5 parts of hydroxylamine hydrochloride together with an equivalent amount of potassium carbonate, and allowing the mixture to remain in the dark at 0° for four to five days. It crystallises in colourless nodules, becomes dark-coloured at 140°, and explodes violently at 155°; it is very sparingly soluble in water and alcohol, somewhat more soluble in chloroform and acetone, and is soluble in acids and alkalis to colourless solutions. After some time, it imparts a yellowish-red colour to a splinter of pine-wood moistened with hydrochloric acid. As this substance must have the formula

$$CH_2<\begin{matrix}C(NOH)\cdot CH_2\\C(NOH)\cdot CH_2\end{matrix}>C:NOH,$$

it follows either that free phloroglucinol has the constitution $CH_2<\begin{matrix}CO\cdot CH_2\\CO\cdot CH_2\end{matrix}>CO$, or if the older constitution $C_6H_3(OH)_3$ is correct, that it readily changes into the isomeric form in the course of reactions. A new system of nomenclature for ketones is described. A. J. G.

Nitrophenyl Benzoate and Nitrobenzoates and their Products of Decomposition. By G. Neumann (*Ber.*, **18**, 3319—3323).—Orthonitrophenylbenzoate is obtained by heating orthonitrophenol with benzoic chloride for 4½ days. It is readily soluble in ether, benzene, and acetone, &c., and crystallises in splendid, large twin crystals melting at 59° (compare Stünkel, *Dissertation Göttingen*, 1880). Nitric acid (sp. gr. = 1·48) acts on it with formation of *orthonitrophenyl metanitrobenzoate*, $C_{13}N_8N_2O_6$. The latter forms whitish-yellow needles, soluble in cold chloroform and hot alcohol, ether, light petroleum, &c. It melts at 126°.

2 : 4 *Dinitrophenyl metanitrobenzoate*, $C_{13}H_7N_3O_8$, is obtained by the action of nitric acid (sp. gr. = 1·53) on orthonitrophenyl benzoate. It

crystallises in small, yellowish needles melting at 161°; it dissolves readily in benzene, acetone, and aniline, less readily in glacial acetic acid and chloroform, and is very sparingly soluble in alcohol, ether, and light petroleum. Strong alcoholic soda converts it into α-dinitrophenol and orthonitrobenzoic acid. N. H. M.

Orthonitroglycines and their Reduction-products. By J. Plöchl (*Ber.*, **19**, 6—11).—*Orthonitrophenylglycin* (nitranilidoacetic acid), $NO_2 \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot COOH$, is prepared by heating orthonitraniline with bromacetic acid in aqueous solution. It crystallises in compact, dark-red prisms, melts at 192—193° with decomposition, and is readily soluble in hot water or hot alcohol, sparingly soluble in ether. It shows pronounced acid properties, yielding well crystallisable salts with bases. The ammonium salt crystallises in lustrous, yellowish-red, flat prisms.

Hydroxydihydroquinoxaline, $C_6H_4<\begin{matrix}-NH\cdot CH_2-\\ N : C(OH)\end{matrix}>$, is obtained by reducing the nitrophenylglycin with tin and hydrochloric acid. It crystallises with 1 mol. H_2O in lustrous, nearly colourless needles or prisms, which melt at 93—94°; the anhydrous base melts at about 130°. It is sparingly soluble in benzene, chloroform, light petroleum, and cold water, moderately soluble in ether, readily soluble in alcohol; it forms salts with both acids and alkalis. The acid solutions on exposure to air acquire a red colour, whilst a red, amorphous substance separates; the alkaline solutions seem to oxidise when exposed to air.

Orthonitrotolylglycin (nitrotoluidoacetic acid),

$NO_2 \cdot C_6HMe \cdot NH \cdot CH_2 \cdot COOH$ [$NH \cdot CH_2 \cdot COOH : NO_2 : Me = 1 : 2 : 4$],

is prepared from the corresponding nitrotoluidine in manner similar to the anilido-compound, which it closely resembles. It is obtained in reddish-brown, prismatic crystals, melts at 189—190° with decomposition, and has marked acid properties.

Hydroxydihydrotoluquinoxaline, $C_9H_{10}N_2O$, prepared by reduction of the preceding compound, closely resembles the base described under the same name by Hinsberg (this vol., p. 82), except that it melts at about 265°, whilst Hinsberg's base melts at 124°.

A. J. G.

Orthonitrotolylglycin: Metanitroparatolunitrile. By R. Leuckart (*Ber.*, **19**, 174—175).—The author, in conjunction with A. Herrman, has independently prepared the orthonitrotolylglycin and its reduction-product, hydroxydihydrotoluquinoxaline, described by Plöchl (preceding Abstract).

Metanitroparatolunitrile, $NO_2 \cdot C_6H_4Me \cdot CN$ [$Me : NO_2 : CN = 1 : 3 : 4$], has been prepared by the author and Holzborn, from metanitroparatoluidine by Sandmeyer's method. It melts at 99—100°.

A. J. G.

Separation of Phenylacetic and Phenylpropionic Acids. By E. Salkowski (*Zeit. physiol. Chem.*, **10**, 150—152).—The separation of the mixture of phenylacetic and phenylpropionic acids obtained from putrefaction-products may be effected as follows:—The oily

liquid is well mixed with a relatively large quantity of zinc oxide and water, and boiled with $1\frac{1}{2}$ to 2 litres of water. On cooling the hot solution, a small quantity of a zinc salt crystallises out. On evaporating the mother-liquor, crystals of another salt form almost to the last drop. The crystals which form first, and that part of the original mixture not dissolved by water, consist of zinc phenylpropionate. The second crystallisation is that of zinc phenylacetate; from these compounds the acids can be respectively obtained and purified.

W. D. H.

Triphenylacetic Acid. By K. Elbs and E. Tölle (*J. pr. Chem.*, **32**, 622—630).—Triphenylacetic acid may be obtained by heating trichloracetic acid with benzene and aluminium chloride; the yield is only 5 per cent. of the theoretical amount; it is a very feeble acid, the salts of the alkaline metals being exceedingly unstable. The *silver salt*, $CPh_3{\cdot}COOAg$, forms a white powder, which decomposes at 90°. The *copper*, *lead*, and *cadmium salts* were also prepared. The *aniline salt*, obtained by adding aniline to an ethereal solution of the acid, forms yellow needles; when heated, it is decomposed into the free acid and aniline. *Sulphotriphenylacetic acid* is formed by heating triphenylacetic acid with fuming sulphuric acid at 100°. The *barium salt*, $<^{-C_6H_4{\cdot}SO_3-}_{CPh_2{\cdot}COO}>Ba + H_2O$, and two *lead salts*, $C_{20}H_{24}SO_5Pb$ and $(COOH{\cdot}CPh_2{\cdot}C_6H_4{\cdot}SO_3)_2Pb$, were prepared. Triphenylacetic acid is but little affected by oxidising agents, and the crude acid may be conveniently purified by heating with an aqueous solution of potassium permanganate.

In the foregoing method of preparing triphenylacetic acid, an organic aluminium compound is formed as a bye-product, which yields two oxidation-products on treatment with chromic mixture. The first of these forms slender, yellowish-red needles, melts at 325°, and may be sublimed unaltered; it has the composition $(C_8H_4O)_n$. The second compound forms citron-yellow prisms, melts at 75°, distils with partial decomposition, has the composition $(C_{12}H_8O)_n$, and is readily soluble in the usual solvents.

A. P.

Preparation of Anisic Acid. By E. v. Meyer (*J. pr. Chem.* [2], **32**, 429).—The method of preparing paramethoxybenzoic acid by the action of methyl iodide on parahydroxybenzoic acid is unsatisfactory. The author proposes to obtain it by acting on the potassium salt of the latter acid with potassium methyl sulphate. The potassium salt of parahydroxybenzoic acid is easily obtained by heating potassium salicylate to 220°, or by dissolving the acid in the requisite amount of potassium hydroxide.

G. H. M.

Benzoylmesitylenic Acids. By E. Louïse (*Bull. Soc. Chim.*, **44**, 418—424).—Ortho- and para-benzoylmesitylenic acids are prepared by heating benzoylmesitylene with the theoretical quantity of chromic mixture for about 30 hours. They may be separated by crystallising the magnesium salts from water, that of the ortho-acid

being very readily soluble in hot and cold water, whilst the para-compound is soluble in hot, but almost insoluble in cold water. *Orthobenzoylmesitylenic acid*, $C_6H_2BzMe_2{\cdot}COOH$ [Bz : COOH = 1 : 2], crystallises from benzene in slender, colourless needles; it is soluble in the usual solvents, and melts at 185°; it readily combines with bases forming salts which crystallise with difficulty, and usually form amorphous powders or gummy masses. The *silver* salt, $C_{16}H_{13}O_3Ag$, was prepared as a white, crystalline precipitate. By heating the acid with phosphoric anhydride, a quinone, $C_6H_4{<}\overset{CO}{CO}{>}C_6H_2Me_2$, is formed, which is identical with the β-dimethylanthraquinone, prepared from β-dimethylanthracene, thus confirming the author's previous views on the constitution of this hydrocarbon (*Bull. Soc. Chim.*, **44**, 182).

Parabenzoylmesitylenic acid, [Bz : COOH = 1 : 4], forms colourless crystals, is readily soluble in the usual solvents, with the exception of water in which it dissolves very sparingly, and melts at 160°. The *potassium* and *sodium* salts were prepared in the form of silky, white masses; the *ammonium* salt forms small, brilliant crystals which lose ammonia in a vacuum. The *silver* salt forms a curdy, white precipitate; it may be crystallised from much boiling water in small, colourless needles; the *barium* salt forms long, colourless needles, and contains 2 mols. of water which it loses at 120°; the *calcium*, *copper*, and *cobalt* salts were also prepared. The acid does not yield any quinone when heated with phosphoric anhydride. A. P.

Constitution of Monochlorophthalic Acid. By A. Rée (*Ber.*, **18**, 3359).—Phosphorus pentachloride converts β-sulphophthalic acid quantitatively into a chlorophthalic acid melting at 148°, identical with that described by Claus and Müller (this vol., p. 247) as β-monochlorophthalic acid. N. H. M.

α-Chlorophthalic Acid. By J. Guareschi (*Ber.*, **19**, 134—135).—By partial oxidation of an acetic acid solution of dichloronaphthalene melting at 107°, the author has obtained *α-chlorophthalic acid*, $C_6H_3Cl(COOH)_2$ [1 : 2 : 3]. This acid crystallises in long, colourless, silky needles melting at 184°: 100 c.c. of water dissolve 2·16 grams of acid at 14°. It is soluble in alcohol and ether, and when heated with phenol and sulphuric acid yields a *phthaleïn* which dissolves in potash to a violet solution. The *silver salt* is microcrystalline. The *anhydride* sublimes in colourless needles melting at 122—123°. This acid is of value in determining the α-position in many naphthalene-derivatives.

Dibromonaphthalene, melting at 130—131°, yields the corresponding *α-bromophthalic acid* melting at 176—178°. L. T. T.

Action of Phenylhydrazine on the Anhydrides of Organic Acids. By B. Hötte (*J. pr. Chem.* [2], **33**, 99—100).—*Phthalylphenylhydrazine*, $C_6H_4{<}\overset{CO}{CO}{>}N_2HPh$, is obtained by heating equal molecular weights of phthalic anhydride and phenylhydrazine at 150°. It forms yellow needles which melt at 177—178°. Boiling potash solu-

tion (or hydrochloric acid at 150°) decomposes it into phenylhydrazine and phthalic acid. Benzoyl chloride acts on it at 160—170° with formation of the *benzoyl-derivative*, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N_2PhBz$, crystallising in white plates which melt at 193°. By the action of 2 mols. phenylhydrazine on 1 mol. phthalic anhydride a *compound*, $C_{20}H_{15}N_3O_2$, is formed with elimination of water and ammonia. It melts at 210°.

Succinylphenylhydrazine, $C_2H_4<\begin{matrix}CO\\CO\end{matrix}>N_2HPh$, crystallises in plates melting at 156°. The author is making experiments with a view to determine which hydrogen-atom of the hydrazine combines with the oxygen of the anhydride. N. H. M.

Quinone-derivatives from Ethyl Succinosuccinate. By A. Hantzsch and K. Loewy (*Ber.*, **19**, 26—30).—Herrmann has shown that ethyl succinosuccinate, which may be regarded as a quinonetetrahydrodicarboxylate, when oxidised, readily yields the dihydrodicarboxylate from which direct substitution-derivatives of quinone can only be obtained with simultaneous elimination of the carboxyl-groups (Abstr., 1882, 714). Ebert endeavoured to oxidise ethyl succinosuccinate with nitrous acid, but only obtained a nitroso-derivative; he, however, obtained evidence confirming the supposition that succinosuccinic acid is a para-compound. As it seemed probable that the dihydro-compound might be more readily oxidised by nitrous anhydride the authors have investigated this reaction.

Ethyl dihydroxyquinonedicarboxylate,

$C_6O_2(OH_2)(COOEt)_2$ [$O_2 : (OH)_2 : (COOEt)_2 = 1 : 4 : 2 : 5 : 3 : 6$],

is obtained by treating an ethereal solution of ethyl quinonedihydrodicarboxylate with carefully purified nitrous anhydride. It is also formed in small quantity by the action of nitrous anhydride on ethyl succinosuccinate. It crystallises in yellow prisms, melts at 151°; it is sparingly soluble in water, alcohol, and ether, more soluble in chloroform; all the solutions have an intense red colour, and are distinguished from those of the dihydro-compound by their fluorescence. Its aqueous solution has an acid reaction, and gives characteristic precipitates with nearly all metallic salts. The metallic derivatives have the general formula $C_6O_2(OM')_2(COOEt)_2$; those of magnesium, manganese, and silver each crystallising with $\frac{1}{2}$ mol. H_2O, and of sodium with 2 mols. H_2O and with 1 mol. C_2H_6O, are described.

A. J. G.

β-Benzoisosuccinic Acid. By W. Kues and C. Paal (*Ber.*, **18**, 3323—3326).—*β-Benzoisosuccinic acid*, $CH_2Bz{\cdot}CH(COOH)_2$, is prepared by adding bromacetophenone (1 mol.) to a cold alcoholic solution of ethyl sodomalonate (1 mol.). The product is poured into water, extracted with ether, and the residue obtained by evaporation of the ether saponified with 6 per cent. potash solution. A crystalline substance remains undissolved in the potash. The new acid is readily soluble in ether, alcohol, and hot acetic acid, and crystallises in slender, white needles. It melts at 178—179° with violent effervescence. The

silver salt, $C_{11}H_8O_5Ag_2$, forms a white, crystalline precipitate sparingly soluble in boiling water. The *phenylhydrazine compound*,

$$N_2HPh : CPh\cdot CH_2\cdot CH(COOH)_2,$$

crystallises in groups of slender, white needles sparingly soluble in ether, almost insoluble in benzene, and readily soluble in alkaline carbonates and mineral acids. It melts at 120°.

When β-benzoisosuccinic acid is heated above its melting point, it is converted into benzoylpropionic acid (compare Abstr., 1882, 1074). *Phenylhydrazinebenzopropionic acid*, $N_2HPh : CPh\cdot CH_2\cdot CH_2\cdot COOH$, crystallises in white needles with a silky lustre, but gradually becomes converted into a yellow resin. It is readily soluble in alkaline carbonates, mineral acids, alcohol, and benzene. It melts at 63—65°.

N. H. M.

β-Benzoisosuccinic Acid. By C. A. Bischoff (*Ber.*, **19**, 95).—In reference to Kues and Paal's paper on the above acid (preceding Abstract) the author points out that he had previously described β-benzoisosuccinic acid (Abstr., 1883, 912). The melting point found was 180°, and not 114° (the melting point of benzopropionic acid) as was then inadvertently stated. L. T. T.

Hydrolysis of Aromatic Sulphonic Acids by means of Superheated Steam. By W. Kelbe (*Ber.*, **19**, 92—94).—In some cases (for instance with aromatic bromosulphonic acids) Armstrong's method of treatment with steam at 100° (Trans., 1884, 148) does not yield satisfactory results. The author finds that in many cases if steam superheated by passing through a red-hot copper tube is used instead of steam at 100°, much better results are obtained. The use of excess of sulphuric acid may then be dispensed with. If salts of the sulphonic acid are employed it is of course necessary to add sulphuric acid to liberate the sulphonic acid, and it is then advisable to use sufficient excess of sulphuric acid to form an emulsion thin enough to allow the free passage of the steam. If the free acid is employed in a moist state sufficient sulphuric acid should be used to bind the water.

Orthobromotoluene and bromo-xylene prepared as above with superheated steam, appear to be much more stable towards oxidising agents than when prepared in the ordinary way. The author is now investigating these apparent discrepancies in properties. L. T. T.

Xylidenesulphonic Acids. By E. Nölting and O. Kohn (*Ber.*, **19**, 137—144).—In continuation of previous papers (Abstr., 1883, 593, and this vol., pp. 57 and 58), other xylidenesulphonic acids are described.

Metaxylidinesulphonic acid,

$$NH_2\cdot C_6H_2Me_2\cdot SO_3H \text{ [Me : Me : } NH_2 : SO_3H = 1 : 3 : 4 : 6],$$

already prepared by Jacobsen and Ledderboge (Abstr., 1883, 593) by sulphonation of xylidine, was also obtained by the nitration and subsequent reduction of metaxylenesulphonic acid. No isomeric acid was obtained. The acid is very stable, the SO_3H-group only

being eliminated by continued heating with fuming hydrochloric acid at 180°. The barium salt crystallises with 2 mols. H_2O. All the following compounds were prepared from acid made by both the above methods to fully prove the identity of these two acids. *Diazo-xylenesulphonic acid*, $C_6H_2Me_2<^{N:N}_{SO_3-}>$, forms a fine white powder which when moist decomposes at 60—70°, and when dry explodes on heating. It forms dyes with phenols and amines; thus β-naphthol gives β-naphtholazo-xylenesulphonic acid, $SO_3H{\cdot}C_6H_2Me_2{\cdot}N:N{\cdot}C_{10}H_6{\cdot}OH$, crystallising in green metallic needles, easily soluble in boiling water, and dyeing silk and wool a very yellow ponceau. *Bromo-xylenesulphonic acid*, $C_6H_2BrMe_2{\cdot}SO_3H$, obtained by heating the diazo-compound with concentrated hydrobromic acid, forms white needles easily soluble in cold water. Ammonia converts the chloride into the *amide*, $C_6H_2BrMe_2{\cdot}SO_2NH_2$, which forms small prisms melting at 189—190°. The bromo-acid is reduced to metaxylenesulphonic acid by sodium amalgam. *Bromoxylidinesulphonic acid*,

$$NH_2{\cdot}C_6HBrMe_2{\cdot}SO_3H\ [Me_2 : NH_2 : SO_3H : Br = 1 : 3 : 4 : 6 : ?5],$$

was obtained by dissolving xylidinesulphonic acid in soda, adding bromine (1 mol.) also dissolved in soda, and acidifying. It forms small, white needles soluble in boiling water. The same acid was obtained by the action of bromine or hydrobromic acid on xylidinesulphonic acid dissolved in glacial acetic acid. No dibromo-derivative could be obtained; further bromination eliminated the SO_3H-group.

In the case of the corresponding para-acids, these two methods give isomeric and not identical compounds.

Paraxylidinesulphonic acid,

$$NH_2{\cdot}C_6H_2Me_2{\cdot}SO_3H\ [Me : Me : NH_2 : SO_3H = 1 : 4 : 2 : 5],$$

already obtained by Witt (*Ber.*, **18**, 2664), is always formed when pure paraxylidine is sulphonated. The *diazo-acid* forms yellowish-white scales which decompose at about 60—70° when moist, and when dry explode on heating. When heated with hydrobromic acid, it forms *bromoparaxylenesulphonic acid*, probably identical with that obtained by Jacobsen by sulphonating bromoparaxylene. The *chloride* of this acid crystallises in small white prisms melting at 77—78°; the *amide* in small white scales melting at 200—201°. No brominated paraxylidinesulphonic acid could be obtained, the sulphonic group being always eliminated, and a *dibromo-xylidine* formed. The same dibromo-xylidine is obtained by the direct bromination of paraxylidine: it forms white needles melting at 65° and yields a crystalline hydrochloride. The above paraxylidinesulphonic acid yields paraxyloquinone when oxidised with chromic acid. There can thus be little doubt of the correctness of the formula ascribed to this acid.

Paraxylidinesulphonic acid, [Me : Me : SO_3H : NH_2 = 1 : 4 : 2 : 6], is obtained, together with traces of the 1 : 4 : 2 : 5 acid, by the nitration and subsequent reduction of paraxylenesulphonic acid. It crystallises with 1 mol. H_2O in sparingly soluble needles. It does not yield a trace of quinone when oxidised. When treated with bromine, it yields a *monobromo-xylidinesulphonic acid* which crystallises from

boiling water in small, silky, white needles. Excess of bromine yields a resinous mass which contains no dibromo-acid or amide, but from which a small quantity of a substance melting at 106—107° was obtained, which appears to be a brominated quinone. The correctness of the formula ascribed to this xylidinesulphonic acid as compared with the only other possible formula, 1 : 4 : 2 : 3, was proved by Skraup's reaction, when it yields a xyloquinolinesulphonic acid, thus showing that there must be one of the hydrogen-atoms next the amido-group still intact. L. T. T.

Action of Ethyl Chlorocarbonate on Phenyl- and Diphenyl-thiocarbamide. By M. Seidel (*J. pr. Chem.* [2], **32**, 261—278).—This work was undertaken in order to ascertain if the thiocarbamides behaved in the same way as the carbamides when treated with ethyl chlorocarbonate.

Ethyl thiodiphenylallophanate, NHPh·CS·NPh·COOEt, is prepared by acting on diphenylthiocarbamide with ethyl chlorocarbonate; it forms white prisms, melts at 95°, and is easily soluble in alcohol, ether, benzene, and chloroform, but insoluble in water. It gives precipitates with metallic salts. When treated with potash or soda the COOEt-group is eliminated, and diphenylthiocarbamide regenerated. Heated with aqueous ammonia, it yields *phenylthiocarbamide*, and with aniline *diphenylthiocarbamide*. Treated with alcoholic ammonia in the presence of mercury oxide, it yields a compound with mercury oxide, $(NHPh\cdot CO\cdot NPh\cdot COOEt)_2HgO$, this forms small prisms and melts at 129°. Ammonia in the presence of lead oxide yields the corresponding lead salt, lead peroxide, however, gives *diphenylthiocarbamide*. When hydrogen sulphide is passed through a solution of the mercury compound in absolute alcohol, mercury sulphide is thrown down, and the ethyl salt is regenerated.

When heated with hydrogen chloride, ethyl thiodiphenylallophanate is decomposed into carbonic anhydride, ethyl chloride, diphenylthiocarbamide, and phenyl isothiocyanate.

Ethyl thiophenylallophanate, NHPh·CS·NH·COOEt, formed by the action of ethyl chlorocarbonate on phenylthiocarbamide, is a yellow oily substance, which after a time sets to a crystalline mass. Warmed with acetic chloride, it yields *acetylphenylthiocarbamide*, the COOEt-group being replaced by the acetyl-group. In order to see if ethyl allophanate behaved in the same way with acetic chloride, the two were heated together in a sealed tube at 80—100° for some hours, *ethyl acetylallophanate*, NHAc·CO·NH·COOEt, was formed; this crystallises in needles, and melts at 107°; it is easily soluble in alcohol, but only slightly in benzene or ether.

Ethyl isothiophenylallophanate, $NH_2\cdot CS\cdot NPh\cdot COOEt$, is formed by heating dry acetylphenylthiocarbamide with an excess of ethyl chlorocarbonate; it forms monoclinic plates, and melts at 127°. This substance requires to be heated in sealed tubes with aqueous ammonia before the COOEt-group is eliminated, thus differing from ethyl thiophenylallophanate, which is split up on gently warming with ammonia. The author points out that the fact of the COOEt- and

acetyl-groups being interchangeable is very unusual in complex organic compounds. G. H. M.

Isatoic Acid. By E. v. Meyer and T. Bellmann (*J. pr. Chem.* [2], **33**, 18—31; comp. Abstr., 1885, 666).—Experiments show that isatoic acid is identical with anthranilcarboxylic acid (Abstr., 1884, 61). The yellow colour of isatoic acid can be removed by oxidising agents, such as nitrous acid. When isatoic acid is boiled with benzoic chloride, benzoylanthranil (Abstr., 1884, 60) is formed.

Anthranil hydroxylamide, $NH_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot OH$, is formed by adding finely-powdered isatoic acid (1 mol.) to a dilute solution of hydroxylamine hydrochloride (2 mols), and sodium carbonate (1 mol); carbonic anhydride is evolved. It forms lustrous, slightly yellow plates, melting at 82°, readily soluble in alcohol, ether, and chloroform. *Amidoanthranilanilide*, $NH_2 \cdot C_6H_4 \cdot CO \cdot NPh \cdot NH_2$, is obtained by the action of phenylhydrazine on isatoic acid, and crystallises in yellow needles, melting at 170°.

When isatoic acid is heated with pyrocatechol at 120—140°, carbonic anhydride is evolved, and *hydroxyphenyl anthranilate*, $NH_2 \cdot C_6H_4 \cdot COO \cdot C_6H_4 \cdot OH$, is obtained. The latter dissolves in alcohol and ether, sparingly in water; it melts at 136°, reduces silver solutions, and gives a dark colour with a solution of ferric chloride.

Formylanthranilic acid, $C_{16}H_{16}N_2O_7$, is obtained by boiling isatoic acid and aqueous formic acid for some hours. A clear solution is obtained, which when poured off and allowed to cool solidifies. This is then warmed to remove any formic acid, and extracted with ether. The ether is evaporated, and the product crystallised from chloroform, from which it separates in hair-like, matted needles, melting at 168°. It dissolves readily in alcohol, sparingly in benzene. It is readily soluble in hydrochloric acid, and the solution, on evaporation, yields anthranilic acid hydrochloride. When distilled with dilute sulphuric acid, it decomposes with formation of anthranilic and formic acids. When heated with water at 130—140°, formic acid, aniline, and carbonic anhydride are formed.

When that portion of the product of the action of formic acid on isatoic acid which did not dissolve in ether is dissolved in warm concentrated hydrochloric acid, and the whole cooled, the *hydrochloride* of a compound, $C_{31}H_{20}N_4O_6$, separates in prisms. When warmed with water, they give up hydrochloric acid; the product crystallises from alcohol in lustrous prisms melting at 280° with decomposition. It is sparingly soluble in alcohol, scarcely at all soluble in water, benzene, chloroform, and ether. Aqueous alkali solutions dissolve it readily; the solution in dilute soda yields a salt crystallising in matted needles. This when treated with acetic acid gave a substance melting at 201°. Hydrochloric acid acts on the compound $C_{31}H_{20}N_4O_6$ with formation of anthranilic acid, and a compound which when warmed with alkali yields phenylcarbylamine.

When a mixture of 15 grams of isatoic acid, 20 grams of phosphorus pentachloride and 10 grams of phosphorus oxychloride is warmed, carbonic anhydride and carbonic oxychloride are evolved, and a compound is obtained which, when treated with ethyl alcohol, yields

prisms melting at 170°. Its composition is expressed by the formula $C_{17}H_{18}N_2O_5$. Hydrochloric acid at 120° decomposes it into anthranilic acid and ethyl chloride. When treated with methyl alcohol, small needles are obtained, which melt at 210° and have the composition $C_{16}H_{16}N_2O_5$.

Bleaching powder suspended in chloroform acts on isatoic acid with formation of an *isomeride*, $C_8H_5NO_3$, crystallising in small, pointed needles, melting at 240°. It is readily soluble in alcohol, acetone, and benzene. Hydrochloric acid precipitates from a solution of the acid in ammonia a new acid melting above 260°.

When acetylisatin is oxidised with chromic anhydride acetylanthranilic acid is formed; acetylisatin is therefore differently constituted to isatin, which under the same conditions yields anthranilcarboxylic acid. N. H. M.

Halogen-derivatives of Isatoic Acid. By R. Dorsch (*J. pr. Chem.* [2], **33**, 32—57).—*Monobromisatoic acid*, $<^{C_6H_3Br}_{CO-}>N\cdot COOH$, is obtained by heating isatoic acid suspended in glacial acetic acid with twice its weight of bromine at 80—100° for an hour. The white, lustrous plates thus formed are collected, washed with glacial acetic acid, and dried at 80°. It melts at 270—275°, dissolves in acetone, sparingly in alcohol and glacial acetic acid, and is insoluble in water, chloroform, ether, &c. When boiled with concentrated hydrochloric acid, it yields metabromorthamidobenzoic acid (m. p. 208°). Hot aqueous ammonia converts it into the amide of the above acid, $NH_2\cdot C_6H_3Br\cdot CONH_2$; this forms broad, white needles, melting at 177°, very readily soluble in alcohol, acetone, and glacial acetic acid, less soluble in water and benzene, insoluble in ether.

When isatoic acid suspended in glacial acetic acid is heated with four times its weight of bromine, 3 : 4 dibromamidobenzoic acid (m. p. 226°) is obtained together with *tribromanthranilic* acid, melting at 119°, and *tetrabromanthranilic acid*, $NH_2\cdot C_6Br_4\cdot COOH$. The latter crystallises in white needles, which melt at 115°, and sublime at 100° in long, slender, lustrous needles.

Monobromonitranthranilic acid, $NO_2\cdot C_6H_2Br(NH_2)\cdot COOH$, is prepared by heating nitroisatoic acid suspended in glacial acetic acid with an excess of bromine at 100°, until no more carbonic anhydride is evolved. On cooling, the new compound separates in long, yellow needles. It melts at 272°, but begins to blacken and decompose at a lower temperature. It dissolves readily in acetone, alcohol, and glacial acetic acid, and is insoluble in benzene and chloroform. The acetic acid mother-liquor when treated with more bromine and evaporated to dryness yields a compound, probably *dibromonitranthranilic acid*, melting at 203°; it dissolves in benzene, chloroform, and ether, more readily in acetone, alcohol, and glacial acetic acid. *Tribromonitranthranilic acid*, $NH_2\cdot C_6Br_3(NO_2)\cdot COOH$, was also found in the mother-liquor; it forms yellowish-white needles which melt at 196°, it is very readily soluble in alcohol, ether, glacial acetic acid, &c.

These experiments show that one hydrogen-atom in isatoic acid is readily replaced by bromine, and that when replaced by bromine or

other radicle, a second atom of bromine cannot be introduced. Chlorine acts slowly on isatoic acid suspended in boiling chloroform, and exposed to sunlight, chlorisatoic acid being formed.

Dibromisatoic acid, $C_7H_2Br_2ON{\cdot}COOH$, is obtained by adding the theoretical amount of chromic anhydride to finely-powdered monobromisatin, suspended in cooled glacial acetic acid. After 12 hours, the whole is warmed at 40—50°, and finally at 60—70° for some hours. The product is then poured into very dilute, cold sulphuric acid, and the yellow crystalline precipitate thus formed crystallised from a mixture of alcohol and acetone. It melts at 255°, and dissolves rather readily in glacial acetic acid and acetone, sparingly in alcohol, chloroform, &c. Hydrochloric acid converts it into dibromanthranilic acid. Ammonia acts on it at 100°, with formation of the *amide*, $NH_2{\cdot}C_6H_2Br_2{\cdot}CONH_2$. This forms sparingly soluble, long, white needles, melting at 196—197°.

Monochlorisatoic acid, $C_7H_3ClON{\cdot}COOH$, is obtained in a manner similar to dibromisatoic acid by the oxidation of chlorisatin, and forms long, lustrous, rectangular plates, melting at 265—268° with evolution of gas. It is sparingly soluble in alcohol, acetone, and glacial acetic acid. When boiled with strong hydrochloric acid, it is converted into *chloranthranilic* acid. The latter forms long, white needles, very readily soluble in alcohol and acetone, soluble in ether and benzene. The solutions are yellowish, and have a violet fluorescence. *Chloranthranilamide* is formed by the action of ammonia on chlorisatoic acid, and crystallises in white needles, melting at 172°, readily soluble in alcohol, acetone, &c., sparingly soluble in chloroform, benzene, and ether.

Dichlorisatoic acid, $C_7H_2Cl_2ON{\cdot}COOH$, forms yellow prisms which melt with evolution of gas at 254—256°; it is readily soluble in acetone and glacial acetic acid. Boiling hydrochloric acid converts it into *dichloranthranilic acid*. This forms small white needles, which melt with partial decomposition at 222—224°; it is readily soluble in the usual solvents. The *amide* crystallises in short white needles, melting at 284° with decomposition.

Nitrobromisatin, $NO_2{\cdot}C_6H_2Br_2{<}^{CO}_{\ N}{>}C{\cdot}OH$, is prepared by treating a solution of bromisatin in concentrated sulphuric acid with potassium nitrate. It forms orange-coloured crystals, melting at 237° with partial decomposition. It is readily soluble in acetone and glacial acetic acid, soluble in alcohol, and sparingly soluble in benzene, chloroform, water, and ether. The solution in cold soda has a dark-red colour.

In converting brom- and chlor-isatoic acids into the corresponding derivatives of anthranilic acid and anthranilamide, metabromorthamido- and parametadibromorthamido-benzoic acids were obtained. It is, therefore, probable that the first bromine-atom substituted in isatin has the meta-position (CO = 1), whilst the second bromine-atom takes up the para-position. When monobrom- and monochlorisatin are distilled with lime, they yield parabrom- and parachloraniline respectively (*Annalen*, **53**, 8). As the first substituted hydrogen-atom is in the para-position to the nitrogen, the second

substituted halogen can only be in the meta-position to the nitrogen. This is contrary to the view expressed by Baeyer (*Ber.*, **15**, 2098).

N. H. M.

Paramethylisatoic Acid and Derivatives of Paramethylisatin. By W. Panaotović (*J. pr. Chem.* [2], **33**, 57—75).—*Paramethylisatoic acid*, $<^{C_6H_3Me}_{CO}>N\cdot COOH$, is prepared by the oxidation of methylisatin in the same way that the halogen-derivatives of isatoic acid are obtained from the corresponding isatin-derivatives (compare preceding Abstract). It is very readily soluble in acetone, from which it crystallises in small, rhombic prisms, soluble in alcohol, ether, and benzene, &c. It decomposes at 245°, but melts only above 300° with evolution of carbonic anhydride. *Nitroparamethylisatoic acid*, $NO_2\cdot C_7H_2MeON\cdot COOH$, is obtained by dissolving methylisatoic acid in cold nitric acid (sp. gr. = 1·48). It forms pale-yellow, rhombic plates melting at 175°, sparingly soluble in water, more readily in alcohol, ether, chloroform, and acetone.

When methylisatoic acid is warmed with hydrochloric acid (sp. gr. = 1·20), it is converted into the hydrochloride of paramethylanthranilic acid melting at 172°, identical with Jacobsen's α-amidometatoluic acid (Abstr., 1882, 185). This, when treated with sulphuric acid and sodium nitrite, yields paramethylsalicylic acid, identical with Jacobsen's parahomosalicylic acid (Abstr., 1878, 582). It melts at 151°.

Paramethylanthranilamide, $NH_2\cdot C_6H_3Me\cdot CONH_2$, is formed by warming methylisatoic acid in aqueous ammonia (sp. gr. = 0·895). Carbonic anhydride is evolved, and the new compound separates as a slightly yellow, lustrous, crystalline mass. It is readily soluble in alcohol, benzene, light petroleum, and ether, and crystallises in colourless, monoclinic prisms melting at 178°.

Paramethylanthranilanilide, $NH_2\cdot C_6H_3Me\cdot CO\cdot NHPh$, is prepared by boiling 2 grams of paramethylisatoic acid, dissolved in the smallest amount of alcohol with 4 grams of aniline. The reaction then begins with violent evolution of carbonic anhydride. When cold, the product is washed with water containing hydrochloric acid, and crystallised from alcohol, from which it separates in colourless, lustrous rhombic plates, melting at 240°; it is readily soluble in chloroform, soluble in ether, light petroleum and benzene, almost insoluble in water. Baryta decomposes it with evolution of carbonic anhydride and formation of barium paramethylanthranilate.

Paramethylanthranilamidoanilide, $C_{14}H_{15}N_3O$, is prepared by warming slightly 2 grams of methylisatoic acid with 3 grams of phenylhydrazine, and forms colourless, rhombic prisms melting at 198°, sparingly soluble in ether, readily in boiling alcohol and chloroform. The solution in concentrated sulphuric acid is violet.

Methyl paramethylanthranilate, $NH_2\cdot C_6H_3Me\cdot COOMe$, is obtained by heating paramethylisatoic acid with methyl alcohol at 180°. It forms long, rhombic prisms, which melt at 62°, and is readily soluble in alcohol, ether, and chloroform.

Acetylparamethylisatin was prepared by boiling methylisatin with acetic anhydride, and has all the properties of Duisberg's

acetylparatolylparamethylpseudoimesatin (Abstr., 1885, 544). Absolute alcoholic ammonia acts on it with formation of *acetylparamethylisatinamide*, $NHAc{\cdot}C_6H_3Me{\cdot}CO{\cdot}CONH_2$. This crystallises in colourless prisms melting at 141°, and is soluble in warm alcohol.

Phenylhydrazine-paramethylisatin, $C_{15}H_{13}N_3O$, forms gold-coloured needles, which sublime at 240° and melt with evolution of gas above 300°. It is readily soluble in alcohol and chloroform.

Diphenylhydrazine-paramethylisatin, $C_{21}N_5H_{19}$, is prepared by the action of phenylhydrazine on acetylparamethylisatin. It is readily soluble in chloroform and alcohol, from which it crystallises in yellow, rhombic prisms, which melt at 255° with decomposition. The corresponding compound obtained from acetylisatin forms long, lustrous, pale-yellow needles, melting at 115°.

The experiments above described show that paramethylisatin and paramethylisatoic acid are completely analogous in their behaviour to isatin and isatoic acid respectively. Paramethylisatoic acid is, therefore, paramethylanthranilcarboxylic acid. N. H. M.

Bases of Methyl-violet and of Magenta. By H. Wichelhaus (*Ber.*, **19**, 107—110).—In a previous paper (Abstr., 1883, 1098), the author showed that methyl-violet, prepared from pure dimethylaniline, contains two bases, which he has now further examined. The salts of the amorphous base formed amorphous glittering masses, varying in colour from yellow to copper-colour. The leuco-base obtained by reduction was too easily reoxidised to be obtained in a pure state. The decomposition-products of the original red amorphous powder were therefore examined. On continued boiling with hydrochloric acid (for about 200 hours), it was completely decomposed into dimethylaniline and *trimethyldiamidobenzophenone*,

$$NHMe{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}NMe_2.$$

This substance crystallises from alcohol in small, white needles melting at 156°, forms a crystalline platinochloride, and yields a hydrole on reduction. It thus appears that the red amorphous base of methyl-violet is *pentamethyltriamidotriphenylcarbinol*.

The crystalline base, when similarly decomposed, yielded dimethylaniline and tetramethyldiamidobenzophenone, already described by Michler and Dupertuis (this Journal, 1877, ii, 333). The base is therefore *hexamethyltriamidotriphenylcarbinol*.

Pararosaniline and rosaniline were also subjected to similar decomposition by boiling with hydrochloric acid. Both yielded the same amidoketone, $CO(C_6H_4{\cdot}NH_2)_2$; the former giving also aniline, the latter toluidine. The ketone crystallises from alcohol in colourless needles melting at 237°. Its sulphate and chloride both crystallise in large flat needles. L. T. T.

α-Iodonaphthalene. By E. Nölting (*Ber.*, **19**, 135—136).—This substance may be prepared by acting on diazonaphthalene sulphate with hydriodic acid, or on an acid solution of the sulphate with potassium iodide. An excess of hydriodic acid must be avoided, or the iodonaphthalene will be reduced to naphthalene. The corresponding

iodobenzene, iodotoluene, iodoxylene, &c., are not reduced by hydriodic acid at its boiling point. L. T. T.

Derivatives of β-Naphthaquinone. By R. Koreff (*Ber.*, **19**, 176—184). — Metallic derivatives of β-naphthaquinonedioxime are readily obtained by adding metallic salts to an ammoniacal solution of the dioxime; one hydrogen-atom only is replaced in these compounds. The silver-derivative, $C_{10}H_7N_2O_2Ag$, is a dark-red precipitate.

The *β-methyl ether*, obtained by the action of methyl iodide on the silver salt, is a clear yellow oil. As it can also be obtained by the action of hydroxylamine on β-nitroso-α-naphthol, it must have the constitution OH·N : $C_{10}H_6$: N·OMe [NOH : NOMe = 1 : 2]. The metallic salts must also be β-derivatives.

The *α-methyl ether*, [NOH : NOMe = 2 : 1], is prepared by boiling an alcoholic solution of α-nitroso-β-naphthol with hydroxylamine; it crystallises in yellow needles, melts at 158—159°, and is insoluble in water, soluble in alkalis.

When β-naphthaquinonedioxime is reduced, it yields the naphthylenediamine described by Griess (Abstr., 1883, 183).

The oxidation-product (m. p. 126°) of β-naphthaquinonedioxime has the formula $C_{10}H_6N_2O_2$, and most probably the constitution $C_{10}H_6\ll^{NO}_{NO}>$. Diphenylglyoxime, OH·N : CPh·CPh : N·OH, when oxidised, yields a similar product, $<^{CPh:NO}_{CPh:NO}>$. This crystallises in flat, lustrous, colourless needles, and melts at 114°. A. J. G.

Juglone. By A. Bernthsen and A. Semper (*Ber.*, **19**, 164—170).—In a previous communication (Abstr., 1885, 546), the authors have shown that juglone is a hydroxynaphthaquinone isomeric with the known hydroxy-α-naphthaquinone, and that on oxidation with nitric acid, juglonic acid (α-dinitrohydroxyphthalic acid) is formed, thus showing that the OH-group and the quinone oxygen-atoms are not in the same ring. Mylius has since confirmed the authors' suggestion, that juglone is an α-naphthaquinone-derivative, so that it must have the constitution [O : O : OH = 1 : 4 : 1′ or 1 : 4 : 2′]. If, as the authors think, the first supposition is correct, then juglonic acid must be a dinitro-derivative of α-hydroxyphthalic acid,

$$[OH : COOH : COOH = 1 : 2 : 3],$$

an acid prepared by Miller from ethyl α-nitrophthalate (Abstr., 1882, 405), and by Jacobsen from 1 : 2 : 3 hydroxytoluic acid (Abstr., 1883, 1124).

α-Hydroxyphthalic acid is best prepared by reducing α-nitrophthalic acid with glacial acetic acid and zinc-dust in the cold. After some time, a voluminous double acetate and amidophthalate of zinc separates, which, after purification, is diazotised in presence of a large excess of sulphuric acid. The α-hydroxyphthalic acid so obtained yields juglonic acid when nitrated, thus fully confirming the authors' supposition that juglone is α-hydroxy-α-naphthaquinone.

Juglonedioxime, $OH{\cdot}C_{10}H_5(N{\cdot}OH)_2$, is obtained by heating juglone with the requisite quantity of hydroxylamine hydrochloride at 140°. It crystallises in brownish-yellow needles, explodes when heated to about 225°, and is far less soluble in alcohol than the monoxime (*loc. cit.*). The formation of this compound affords fresh proof of juglone being an α-quinone, inasmuch as Goldschmidt has shown that β-naphthaquinone yields not a dioxime, but the corresponding anhydride (Abstr., 1884, 735).

Juglonic acid has been obtained in the crystalline form.

A. J. G.

Isomeric α-Naphthylaminesulphonic Acids. By O. N. Witt (*Ber.*, **19**, 55—59).—The author has compared Piria's naphthionic acid (*Annalen*, **78**, 31), the amidonaphthalenesulphonic acid obtained by Nevile and Winther by heating naphthylamine with sulphuric acid (equal mols.) at 180—200° (Trans., 1880, 632), and the acid prepared technically by dissolving naphthylamine (1 part) in sulphuric acid (5 parts), and finds that all three are identical. A. J. G.

Conversion of Terebenthene into an Active Terpilene. By G. Bouchardat and J. Lafont (*Compt. rend.*, **102**, 50 — 52).—1200 grams of terebenthene boiling at 155—157° was dissolved in glacial acetic acid and gradually mixed with 880 grams of chromic acid also dissolved in acetic acid, care being taken to keep the temperature below 40°. No carbonic anhydride is evolved, and the greater part of the terebenthene remains unoxidised, but undergoes other modification. The products boiling below 190° can be separated into two fractions, one boiling at 155—156°, the other at 174—178°. The first is a mixture of the original terebenthene with a certain proportion of camphene; the second has the odour of essence of citron, and resembles it in its principal properties. It has the composition $C_{10}H_{16}$; sp. gr. at 0° (when mixed with about 17 per cent. of cymene) = 0·8672; specific rotatory power $[\alpha]_D = -56$. When treated with a current of dry hydrogen chloride, it yields a crystalline dihydrochloride, which melts at 47°, and has no action on polarised light. If heated with water or alcoholic potash, this dihydrochloride yields a mixture of the hydrocarbon $C_{10}H_{16}$ with terpinol.

If a correction is made for the amount of cymene (about 17 per cent.) mixed with this lævogyrate terpilene and derived from the alteration of the terebenthene, the specific rotatory power of the terpilene will be about $[\alpha]_D = -65$. This terpilene occupies a place in the bivalent series similar to that occupied by the active camphenes in the univalent series. C. H. B.

Synthesis of an Inactive Borneol. By G. Bouchardat and J. Lafont (*Compt. rend.*, **102**, 171—173).—Terebene is heated for 30 hours at 150° with one and a half times its weight of glacial acetic acid, the product mixed with water, washed with a dilute alkaline solution and fractionated. It yields unaltered terebene and terebene acetate, $C_{10}H_{16},C_2H_4O_2$ (borneol acetate). This compound is a colourless, somewhat mobile, neutral liquid, with an odour resembling that of oil of thyme. It boils at 215° without decomposition, and has

no action on polarised light; sp. gr. at 0° = 0·977. When heated in sealed tubes at 100° for 10 hours with its own weight of potassium hydroxide dissolved in alcohol, it yields potassium acetate and an inactive borneol.

The inactive borneol or camphenol thus obtained crystallises completely at the ordinary temperature, and has a pungent camphoraceous odour resembling that of borneol from *Dryabalanops camphora*. It sublimes easily at 100°, melts at about 190°, and boils without decomposition at 208—211° under ordinary pressure. When oxidised with nitric acid, it yields an inactive camphor, and when heated with concentrated hydrochloric acid in sealed tubes at 100° it is converted into a hydrochloride which seems to be identical with that derived from terebene or inactive camphene. C. H. B.

Pimaric Acids. By A. Vesterberg (*Ber.*, **18**, 3331—3334).—When galipot is washed several times with cold 70 per cent. alcohol, and then crystallised from 80 per cent. alcohol at a temperature not above 60°, an acid is obtained melting at 130—140°. This substance has already been prepared by Cailliot (this Journ., 1874, 457), who described it as pimaric acid. When dissolved in dilute soda solution, a sodium salt crystallising in large, thin, lustrous plates is obtained; this yields an acid melting at 210—211° (uncorr.), probably identical with Cailliot's dextropimaric acid (*loc. cit.*). It is insoluble in water, but soluble in hot alcohol and glacial acetic acid, from which it separates in large, rectangular plates. A saturated alcoholic solution at 15° is dextrorotatory $[\alpha]_D = +72{\cdot}5°$. It dissolves sparingly in hot ammonia, readily in potash and soda solutions. The *calcium salt*, $(C_{20}H_{29}O_2)_2Ca$, crystallises in slender needles. Several other salts were prepared. The *ethyl salt* melts at about 46°.

Besides the above, the solution of pimaric acid yielded two more acids, the one melting at 150°, possibly identical with Cailliot's pyromaric acid; the other corresponding with Cailliot's "slightly lævorotatory" acid. The author thinks it probable that Haller's pimaric acid (Abstr., 1885, 1241) consists chiefly of this acid.

It is probable that all three acids pre-exist in the resin, and that the acid described by Cailliot and by the author as "pimaric acid" is therefore a mixture of them. N. H. M.

Volatile Constituents of Ranunculaceous Plants. By H. Beckurts (*Chem. Centr.*, 1885, 776—778).—The author has examined the volatile constituents of *Anemone nemorosa*, *Anemone pratensis*, and *Anemone pulsatilla*. By distillation with water, and subsequent treatment of the distillate with chloroform, *anemone-camphor*, *anemonin*, *anemonic acid*, and a *yellowish oil* were obtained.

Anemone-camphor crystallises in hard, shining, rhombic prisms which do not melt, but evolve water at 150°, and char above 300°. It has a powerful, irritating odour, and a vesicating action. The solutions of the substance spontaneously decompose, yielding a compound soluble in chloroform, and anemonic acid insoluble in chloroform and water. This is noticed in preparing the compound from the plants; the distillate rapidly becomes turbid from the separation of

anemonic acid. The loss of acridity in the plant when kept, and in the pharmaceutical preparations of pulsatilla, is due to the same cause.

Anemonin, $C_{15}H_{12}O_6$, forms odourless, rhombic crystals, melting at 150°. It is soluble in chloroform, less soluble in alcohol and water, insoluble in ether. Anemonin distils with steam, and the aqueous solution reduces gold, platinum, and silver salts. It is unacted on by acetic acid and by benzoic and phosphoric chlorides, but is decomposed when boiled with hydrochloric acid, forming a dark-red, highly fluorescent liquid which when evaporated leaves an amorphous, hygroscopic mass having the properties of an acid. The salts are amorphous, and difficult to purify. This acid, which has the formula $C_{15}H_{14}O_7$, is formed from anemonin by the assimilation of a molecule of water.

Anemonic acid is a yellowish-white, amorphous powder, insoluble in water, alcohol, and ether.

The *yellowish oil* has a sharp, irritating smell, and is a powerful vesicant. It gradually solidifies, forming a hard, white, horny mass without odour, which is resolved by alcohol into anemonin and anemonic acid. W. R. D.

Solubility of Salicin. By D. B. Dott (*Pharm. J. Trans.* [3], **16**, 621—622).—In determinations of solubility, the author urges the importance of conducting the preparation of the solution and the determination at the same temperature. His own experiments with salicin show that solutions prepared at a high temperature and allowed to cool (method "by cooling"), always, even after several days, indicated greater solubility than solutions prepared "by digestion" at an approximately constant temperature. One part of salicin dissolves in 34·74 parts of water at 0°, and the solubility increases with the temperature, directly, up to about 50° (being 1 in 11·50 at 48°), but from this point at a slower rate; at 102° the solubility is 1 in 0·68. D. A. L.

Quercetin and Rhamnetin. By C. Liebermann (*Ber.*, **18**, 3414—3417).—A controversial paper in reply to Herzig (this vol. pp. 251, 252).

Cyclamin and Saponin. By A. Hilger and L. Mutschler (*Arch. Pharm.* [3], **23**, 831—832).—Cyclamiretin was prepared by the action of hydrochloric acid on cyclamin. When fused with potash in an iron retort, a semi-fluid, resinous mass distils over along with drops of oil. On redistilling this product with steam, a small quantity of yellow oil is obtained having the composition C, 85·5; H, 11·2; O, 3·3. The residue exactly resembles colophony, and has nearly the composition $C_5H_7O_2$. This residue gives by dry distillation, either with zinc-dust or alone, an oil similar to the one mentioned above, whilst the distillation residue partly dissolves in alcohol with a bluish-green fluorescence. The residue from the potash fusion, when dissolved in water and acidified with dilute sulphuric acid, gives a slight flocculent precipitate similar to the resin already described. The acidified aqueous solution on distillation gives a distillate smelling

strongly of butyric and formic acids. *Saponin*, a glucoside closely related to cyclamin, when treated similarly, yielded a small quantity of resin and butyric acid, but neither formic acid nor liquid oil.

J. T.

Chlorophyll from the Deep Sea. By W. N. Hartley (*Proc. Roy. Soc. Edin.*, **119**, 130—136).—Specimens of spirit of a fine green colour poured off from shells collected by the "Challenger" expedition, when examined by the spectroscope showed the presence of chlorophyll in solution. Green seaweed brought up on trawls also contained chlorophyll. There seems to be no grounds for supposing that because chlorophyll has been found at depths of 553 fathoms, therefore light has not penetrated so far, and has not operated in its formation, as the photographic tests yet applied are not satisfactory.

E. W. P.

Action of Potash on Boiling Pyrroline. By G. Ciamician and M. Dennstedt (*Ber.*, **19**, 173—174).—The potassium-derivative of pyrroline can be obtained by heating pyrroline with solid potash; this was noticed by Anderson but has since been overlooked. The fact can be utilised in obtaining pyrroline from animal oil as follows:—The fraction containing pyrroline is heated with a large excess of potash in a reflux apparatus until the whole mass is fused, any unchanged oil is separated, and the solid, finely-powdered, crystalline mass washed with anhydrous ether, then treated with water and distilled with steam; the pyrroline so obtained boils at 130—131°. Soda cannot be substituted for potash in the above operation.

A. J. G.

Condensation Products of Pyrroline with Alloxan. By G. Ciamician and P. Magnaghi (*Ber.*, **19**, 106—107).—Meyer and Stadler have shown (Abstr., 1884, 1045) that pyrroline reacts with compounds containing more than one carbonyl-group to form dyes. The authors find that, with alloxan, pyrroline forms in addition a crystalline substance. By treating a solution of 11 grams of alloxan in 300 c.c. of lukewarm water with 5 grams of pyrroline, this crystalline substance is almost exclusively formed, and is gradually deposited from the solution. When pure, it forms small and almost colourless crystals, nearly insoluble in ether, benzene, and cold water, sparingly soluble in alcohol and boiling water. When heated, it is decomposed without previous fusion. It has the formula $C_8H_7N_3O_4$, and when treated with potash evolves ammonia, and forms an unstable crystalline compound which is now under investigation.

L. L. T.

Conversion of Pyrroline into Pyridine. By M. Dennstedt and J. Zimmermann (*Ber.*, **18**, 3316—3319).—When equal molecular weights of sodium (dissolved in the smallest quantity of methyl alcohol), pyrroline and methylene iodide are heated for five hours at 200°, a dark-brown resinous mass is obtained. This is treated with hydrochloric acid and distilled with steam. The residue is made alkaline, distilled with steam, and the distillate extracted with ether. On evaporating the ether, a very small quantity of pyridine is obtained. This was identified by crystallographic measurements of the platinochloride.

This formation of pyridine from pyrroline supports the constitution $NH<\begin{matrix}CH:CH\\CH:CH\end{matrix}>$, ascribed by Baeyer to the latter compound.

N. H. M.

Action of Acetic Chloride on Pyridine. By M. Dennstedt and J. Zimmermann (*Ber.*, **19**, 75—78).—This reaction leads to the formation of dehydracetic acid; the acid is formed from the acetic chloride, the pyridine probably only acting by removing the elements of hydrogen chloride. Picoline and acetic chloride also yield dehydracetic acid. The authors have endeavoured to obtain dehydracetic acid from acetic chloride by passing its vapours through glass or iron tubes heated to various temperatures, or by heating it in sealed tubes, or by heating it with lead oxide, but in all cases without success. A. J. G.

Hydroxylation of Pyridine-derivatives. By J. Messinger (*Ber.*, **19**, 196—197).—When benzylidinecollidinecarboxylic acid is treated with bleaching powder and boric acid, a micro-crystalline substance is obtained, which from its properties must be regarded as a pyridine-derivative in which a hydroxyl-group has been introduced into the side-chain. This compound when treated with dilute hydrochloric acid is converted into a crystalline substance of the formula $C_{17}H_{13}O_4N + 2H_2O$. A. J. G.

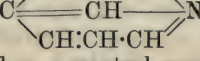
Böttinger's Pyridinedicarboxylic Acid. By C. Böttinger (*Ber.*, **18**, 3461).—A reply to Voges (this vol., p. 257).

Supposed Optical Rotatory Power of Picoline. By H. Landolt (*Ber.*, **19**, 157—158).—Hesekiel has recently stated that synthetically prepared β-picoline is optically active ($-0{\cdot}26°$), thus furnishing an exception to the van't Hoff hypothesis, as picoline does not contain an asymmetric carbon-atom (this vol., p. 256). A similar observation on β-picoline from bone-oil was made by Wiedel (Abstr., 1880, 269). As this observation, if correct, would be of great importance, not only in regard to the van't Hoff theory, but also to the fact that no other substance prepared directly from inactive materials has shown optical rotatory power, the author has repeated Hesekiel's experiments. The β-picoline showed seemingly a slight dextrorotatory power; further examination, however, showed this rotation to be due to the glass plates closing the ends of the tube in which the liquid was contained, these being subjected to considerable pressure by the caps fixing them to the tube. An examination of picoline in tubes, the glass plates of which were not so affected, showed it to be absolutely destitute of rotatory power. Attention has been already drawn by Scheibler (*Ber.*, **1**, 268) to the facts that glass plates may be rendered doubly refractive by pressure, that a good many samples of glass are doubly refractive under ordinary conditions, and, therefore, that the tubes should always be tested before use. As the refractive power of picoline observed by Hesekiel and by Weidel was less than that which can be caused in some cases by

pressure on glass plates, it seems very probable that it may be due to this cause. A. J. G.

Action of Acetophenone on Ammonia. By C. Engler and P. Riehm (*Ber.*, **19**, 40—42).—By the action of ammonia on acetophenone in presence of phosphoric anhydride, Engler and Heine obtained a basic substance, to which they assigned the formula $C_{24}H_{19}N$ (this Journ., 1873, 1036). Further investigation has shown this substance to be in all probability a pyridine-derivative of the formula $C_{23}H_{17}N$ ($?C_5NH_2Ph_3[Ph_3 = 2 : 4 : 6]$). The numbers given in the earlier paper agree much better with the new than with the old formula. The investigation is proceeding. A. J. G.

Ammonium-derivatives of Ethereal Salts of Pyridine- and Quinoline-carboxylic Acids. By A. Hantzsch (*Ber.*, **19**, 31—40). *Methyl nicotinate methiodide*, $C_5NH_4{\cdot}COOMe,MeI$, is prepared by the action of excess of methyl iodide on potassium nicotinate; when treated with silver chloride, and subsequently with platinum chloride, the platinochloride $C_{16}H_{20}N_2O_4,PtCl_6 + H_2O$ is formed. The corresponding hydroxide could not be obtained; as when the salts are treated with silver oxide, the betaïn derived from the ammonium hydroxide corresponding to the free acid is obtained.

The *methylbetaïn* of *nicotinic acid*,  $+ H_2O$,

crystallises in long, lustrous needles, has a neutral reaction, and is very readily soluble in water, less soluble in alcohol, and insoluble in the other ordinary solvents. The anhydrous compound melts at 218° with decomposition. The platinochloride, $(C_7H_7NO_2)_2,H_2PtCl_6$, crystallises both in the anhydrous form and with 1 mol. H_2O. The betaïn is not decomposed by boiling with strong sulphuric acid, nor by heating with hydrochloric acid at 260°. By boiling with aqueous potash or baryta, it is decomposed into methylamine and an acid not yet isolated.

The *betaïn* of *collidine-β-carboxylic acid*, $C_{10}H_{13}O_2N$, prepared in manner similar from the methiodide of the methyl salt, crystallises with 3 mols. H_2O, and is completely decomposed at 200°.

A similar compound, $C_6H_7NSO_3$, is obtained by treating potassium pyridine-β-sulphonate with methyl iodide at 150°, and decomposing the product with water.

A betaïn was prepared in a similar manner from picolinic acid; it is crystalline, deliquescent, and gives a platinochloride,

$$(C_7H_7NO_2)_2,H_2PtCl_6.$$

The *methiodide* of *ethyl α-lepidine-β-carboxylate* crystallises in golden needles, melting with decomposition at 205°. The platinochloride, $(C_{13}H_{13}O_2NMe)_2PtCl_6$, crystallises in golden-yellow plates, and melts with decomposition at 216—218°. The methiodide behaves quite differently from those of the pyridine series, described above, when treated with silver oxide, yielding a substance whose reactions best agree with those of an ammonium oxide, $O(C_{14}H_{16}O_2N)_2$. When

treated with dilute acids, it dissolves with re-formation of the salts of the ammonium base. A. J. G.

Quinoline-aldehyde. By W. v. Miller and J. Spady (*Ber.*, **19**, 130—134).—The results given in Einhorn's paper on this subject (this vol., p. 264), differing in many points from those previously given by the authors (this vol., p. 264), they have repeated those parts of both their own and Einhorn's work where discrepancies arise, and have found that their results are correct. L. T. T.

Bye-products of Quinaldine. By O. Doebner and W. v. Miller (*Ber.*, **18**, 3352—3353).—The fraction of crude quinaldine (freed from aniline, monethylaniline, and tetrahydroxyquinaldine by means of nitrous acid), boiling at 270—280°, was identified as trimethylquinoline. This is probably formed by the action of 3 mols. of aldehyde on aniline (comp. this vol., p. 264). N. H. M.

Action of Hypochlorous Acid on Quinoline-derivatives. By A. Einhorn and R. Lauch (*Ber.*, **19**, 53—55).—When quinoline is treated with an aqueous solution of hypochlorous acid, much heat is evolved and carbosytyril is formed. By mixing quinoline borate with a well-cooled aqueous solution of bleaching powder, a substance of the formula C_9NH_6OCl is formed; it crystallises in long white needles, and melts at 112°. This substance can also be obtained by treating the potassium-derivative of carbostyril with sodium hypochlorite. When dissolved in alkalis, and precipitated with carbonic anhydride, carbostyril is again obtained. A. J. G.

Quinoline-derivatives from Isatinic Acid. By W. Pfitzinger (*J. pr. Chem.* [2], **33**, 100).—Acetone reacts with isatinic acid in alkaline solution, with elimination of 2 mols. of water, and formation of a methylquinolinecarboxlic acid, melting at 240—241,° probably identical with aniluvitoninic acid, obtained by Böttinger (*Ber.*, **15**, 2357) from aniline and pyruvic acid. N. H. M.

Dimethylnaphthaquinoline. By J. H. Reed (*J. pr. Chem.* [2], **32**, 630—631).—A dimethylnaphthaquinoline, $C_{15}NH_{13}$, may be prepared by treating acetone, paraldehyde, and β-naphthylamine with hydrochloric acid; it is a white, crystalline substance, melts at 126—127°, and distils at above 360°. The *picrate*, $C_{15}H_{13}N,C_6H_2(NO_2)_3{\cdot}OH$, form small yellow needles, sparingly soluble in acetone and alcohol. The *dichromate* forms small, reddish-yellow needles, melts with decomposition at 115°, and is sparingly soluble in boiling water, but dissolves readily if a small amount of sulphuric acid is added. A. P.

Sparteïne and its Salts. By A. Houdé (*J. Pharm.* [5], **13**, 39—41).—The leaves and branches of *Spartium scoparium* are lixiviated with alcohol at 60°, until the washings cease to give a precipitate with iodated potassium iodide. The alcoholic solution is distilled under diminished pressure at a low temperature, and the residue is taken up with a solution of tartaric acid. After filtration, the solution

is rendered alkaline by means of potassium carbonate, and is agitated with ether. Fresh tartaric acid solution is added, the sparteïne again set free by alkali, and taken up by ether; and this treatment is repeated until a colourless, ethereal solution is obtained, which yields pure sparteïne when evaporated without exposure to air or light. A kilogram of plant yields about 3 grams of the pure product. Sparteïne is a colourless liquid boiling at 287°. It is soluble in alcohol, ether, and chloroform, but insoluble in benzene and petroleum. It gives abundant white fumes in presence of hydrochloric acid. It is a tertiary diamine. Easily crystallisable salts are obtained by combining it with acids. Potash and ammonia give a white precipitate with a solution of the sulphate; this precipitate is insoluble in excess: hydrogen carbonate produces no precipitate in the cold, but when heated a whitish deposit forms. Concentrated hydrochloric, nitric, or sulphuric acids produce no coloration with the alkaloïd. Cadmium iodide gives a white curdy precipitate. Sodium phosphomolybdate gives a white precipitate, soluble on heating. Copper salts give a greenish precipitate, platinum chloride gives a yellow crystalline precipitate. J. T.

Quinine Hydrate. By F. W. Fletcher (*Pharm. J. Trans.* [3], **16**, 385).—Quinine retains only 1 mol. H_2O when it is precipitated by ammonia, and dried in the air at the ordinary temperature, or when it is deposited from its solution in ether, and dried either in the air or over sulphuric acid at the ordinary temperature. D. A. L.

Preparation of Cocaine. By E. R. Squibb (*Pharm. J. Trans.* [3], **15**, 774—776, and 796—798).—The following process, which is obviously only approximate, is suggested for the estimation of cocaine in coca-leaves. 50 grams of the finely powdered leaves is moistened with an equal weight of a mixture of 60 parts of alcohol (92 per cent.) and 1 part by weight of sulphuric acid. After a short interval, the mass is percolated with alcohol until 250 c.c. of liquid has been obtained. This is evaporated at as low a temperature as possible to 10 c.c., when about 50 c.c. of water is added in small quantities at a time to extract the soluble matter, including the cocaine salt, and separate chlorophyll and resin. The filtered solution is twice extracted with ether, solution of sodium carbonate then added, and the free cocaine removed from the alkaline liquid by agitation with ether. The ethereal solution is evaporated, the residue superficially washed with a little water, and finally dried and weighed. The residue contains, on an average, about 20 per cent. of alkaloïd with much impurity.

The author has modified this process and applied it to the preparation of the pure alkaloïd on the large scale. Full details of the process, which is long and tedious, are given in the paper, as well as much general information about cocaine and its properties.

W. R. D.

Extraction of Cocaine. By A. Castaing (*Chem. Centr.*, 1885, 927).—One part of the powdered leaves is boiled with eight parts of

water, macerated for half an hour, then percolated. As soon as the liquid has passed through, the leaves are further percolated with eight parts of alcohol. The liquid is precipitated with lead acetate, and the excess of lead removed from the clear liquid by sodium sulphate. This solution, after evaporation to a syrup, is diluted with water, filtered from resin, and precipitated with sodium carbonate. The precipitate is extracted with ether, which on evaporation leaves impure cocaine. This is purified by washing with alcohol, when prisms of cocaine remain. By this method the author obtains 0·2 per cent. of cocaine. The alkaloïd is soluble in 700 parts of cold water, more soluble in alcohol and ether. It is decomposed at 113°. W. R. D.

Wrightine (Conessine). By H. Warnecke (*Ber.*, **19**, 60—62).—*Wrightine*, or *conessine*, was obtained as an amorphous substance by Stenhouse (*Pharm. J. Trans.* [2], **5**, 493) and by Haines (*ibid.* [2], **6**, 432) from the bark of *Wrightia antidysenterica*. The author has extracted this alkaloïd from the seeds of the plant, and has obtained it in a pure condition. It forms a voluminous mass of brittle, colourless needles, of bitter taste. When heated, it turns yellow at 60—70°, and melts at 122° (uncorr.); by further cautious heating, it can be sublimed in part unchanged. It forms crystalline salts with acids, is sparingly soluble in water, readily in alcohol, ether, chloroform, &c. Several colour reactions for the alkaloïd are described, as also an oxidation product not yet obtained in a pure state. From analyses of the free base and of the platinochloride, the author gives the formula $C_{11}H_{18}N$ (compare next Abstract). A. J. G.

Conessine (Wrightine). By K. Polstorff and P. Schirmer (*Ber.*, **19**, 78—85).—The authors have prepared this alkaloïd from the bark of *Holarrhena Africana*, which contains about 0·1 per cent. *Conessine* (*wrightine*), $C_{12}H_{20}N$, crystallises in brittle, silky needles, and melts at 121·5°. The hydrochloride, $C_{12}H_{20}N,HCl + H_2O$, crystallises in groups of needles; the platinochloride, $(C_{12}H_{20}N)_2,H_2PtCl_6 + \frac{1}{2}H_2O$, forms reddish-yellow needles; the aurochloride, $2(C_{12}H_{20}N,HAuCl_4) + 3\frac{1}{2}H_2O$, crystallises in long, golden-yellow needles; the mercurichloride, $C_{12}H_{20}N,HHgCl_3$, also crystallises in needles.

Methylconessine iodide, $C_{12}H_{20}MeNI + 1\frac{1}{2}H_2O$, prepared by heating conessine with methyl iodide and absolute alcohol at 100°, crystallises in pale-yellow tables, readily soluble in hot water. The ethyl compound, $C_{12}H_{20}EtNI + \frac{1}{2}H_2O$, crystallises in pale yellowish-red tables.

Methylconessine hydroxide, obtained by the action of freshly precipitated silver oxide on the iodide, forms a fibro-crystalline mass of strongly alkaline properties; it could not be purified. It eagerly absorbs carbonic anhydride from the air. The normal carbonate, $CO(O\cdot C_{12}H_{20}MeN)_2 + 4H_2O$, crystallises in long brittle needles; an acid carbonate also exists. The chloride, $C_{12}H_{20}MeNCl + 2\frac{1}{2}H_2O$, prepared by the action of hydrochloric acid on the carbonate, crystallises in lustrous, white groups of needles. When the hydroxide is heated at 150° for some hours, it is resolved into conessine and methyl alcohol. If heated directly over a small flame, water and ammonia are given off, and the residue, after treatment with hydrochloric acid,

yields the hydrochlorides of two bases. The free base from the less soluble of these crystallises in needles and melts at 74°.

A. J. G.

Ptomaïne from Poisonous Cheese. By V. C. Vaughan (*Zeit. physiol. Chem.*, **10**, 146—149).—In 1883-4, in Michigan, 300 persons were taken ill after partaking of certain cheeses; the symptoms were vomiting and purging, followed by signs of cardiac failure and great nervous prostration. The cheeses were found to have normal taste and smell, but, when cut, a slightly opalescent acid fluid exuded. Dogs and cats refused to eat the cheese. Microscopic examination revealed numerous micrococci. These were cultivated and injected into rabbits with negative results. A watery extract of the cheese was acid, sodium hydroxide gave a precipitate; this was extracted with ether, evaporated to dryness, dissolved in water, and extracted again with ether. This last ethereal extract was dried in a vacuum over sulphuric acid, when needle-like crystals separated. By experiments on men, this was found to cause symptoms similar to those mentioned above, and was therefore the poison. It was called *tyrotoxicon*; it forms Prussian blue with ferric chloride and ferrocyanide of potassium, and reduces iodic acid. It is not precipitated by the usual precipitants of alkaloïds. 16 kilos. of one cheese yielded 0·5 gram, of another 0·1 gram of tyrotoxicon.

W. D. H.

Coagulation of Albumin. By E. Varenne (*Compt. rend.*, **102**, 129—131).—Egg albumin, prepared by Wurtz's process, coagulates in two phases at 60° and 75° respectively, the first characterised by a turbidity, and the second by the separation of distinct flakes. Solution of white of egg in water coagulates at the same temperatures. Coagulation is materially affected by the presence of various metallic salts, and takes place in one or two phases (corresponding with the two phases in the case of pure albumin) according to the nature and proportion of the salt present.

Ammonium molybdate, potassium chlorate, sodium sulphate, and manganese sulphate exert very little effect, but coagulation takes place in one phase only.

Sodium chloride, magnesium sulphate, sodium thiosulphate, potassium iodide, mercuric potassium iodide, sodium arsenate, sodium borate, and ferric sulphate retard coagulation, or in some cases prevent it completely, if added in sufficient quantity. The last four completely prevent coagulation if present in the proportion of 0·1, 0·5, 0·5, and 0·001 gram per litre respectively.

Cadmium sulphate, uranium acetate, copper sulphate, barium chloride, barium nitrate, urea nitrate, and tartar emetic accelerate coagulation.

C. H. B.

Amido-acids Resulting from the Decomposition of Proteids. By E. Schulze and E. Bosshard (*Zeit. physiol. Chem.*, **10**, 134—145).—In the decomposition of conglutin, amido-acids are obtained which are optically inactive if baryta-water is employed at a temperature of 150—160°, optically active if hydrochloric acid is used. Leucine obtained by the latter method was heated with baryta-water under

pressure at 170° for six hours, when its rotatory power was lessened by one-third; on being heated for three days at 150—160°, it became optically inactive, and its solubility in water diminished. Heating leucine with water for a similar length of time produced no change in it. Changes in the rotatory power of amido-acids are also brought about by fungi; *Penicillium glaucum* was grown in solutions of leucine and glutamic acid, and after five or six weeks the solutions were examined with the polarimeter. It was found that leucine, which is normally dextro-rotatory ($\alpha_D = + 17{\cdot}3$) was converted into an isomeric substance which was lævorotatory ($\alpha_D = - 17{\cdot}3$). Optically inactive leucine was similarly converted into a lævorotatory isomeride. With glutamic acid, similar results were obtained. By the growth of the fungus, this substance, which is normally dextrorotatory ($\alpha_D = + 31{\cdot}6$), was changed into a lævorotatory isomeride ($\alpha_D = - 32{\cdot}3$). Optically inactive glutamic acid was similarly acted upon.

W. D. H.

Venous Hæmoglobin Crystals. By M. Nencki and N. Sieber (*Ber.*, **19**, 128—130).—It is well known that the crystals of arterial hæmoglobin or oxyhæmoglobin show the two characteristic absorption bands, but hitherto no crystals have been obtained of the reduced or venous hæmoglobin. The authors have now succeeded in obtaining crystals of this *venous hæmoglobin*, and find that it shows the characteristic single band of venous blood.

Pure crystallised oxyhæmoglobin from horse blood was dissolved in lukewarm water, a few c.c. of putrefying blood added, and the whole sealed up in a flask from which all the air had been previously expelled by hydrogen. After remaining at 20—25° for 8 to 14 days, by which time every trace of remaining oxygen had been used up by the bacteria, about 25 per cent. of absolute alcohol was added, precautions being taken not to admit air. The solution was now left for 12—24 hours at 5—10°, when venous hæmoglobin crystallised out in glistening hexagonal plates and in prisms, which are violet by reflected, green by transmitted light. Under the spectromicroscope they show the characteristic single band. The prismatic crystals are double-refracting. The examination must be made in the mother-liquor and at low temperatures, as the crystals are very unstable; they deliquesce at the ordinary temperature, and are immediately converted into oxyhæmoglobin by contact with the air. This venous hæmoglobin is more soluble in water than the corresponding oxyhæmoglobin.

The authors state that if horse blood is allowed to putrefy in well-closed vessels, alcohol then added, and the whole allowed to remain for some time at about 0°, venous hæmoglobin separates out in considerable quantity in the form of a crystalline magma. They are now examining the venous hæmoglobin obtained from blood from other sources.

L. T. T.

Physiological Chemistry.

Chemistry of the Retinal Rods. By H. Dreser (*Zeit. Biol.*, **22**, 23—39).—Kühne has previously shown that oxidising agents, including ozone and hydrogen peroxide, have no effect on visual purple (rhodopsin). He had not found it possible to test the effect of osmic acid, because the rods contain a substance, myeloïd, which is coloured black by osmic acid, and this conceals the behaviour of visual purple. Unna found that this black colour is destroyed by hydrogen peroxide. Hence the investigation of the action of osmic acid on visual purple is now possible.

Frogs' retinæ were treated with hydrogen peroxide, and the excess removed by washing with weak soda solution. Osmic acid was added, and within two minutes the purple colour was destroyed. Other frogs' retinæ were allowed to remain over night in a concentrated solution of ammonium chloride; this dissolves out the myeloïd; osmic acid was then added and again destroyed the purple in two minutes. Rabbits' retinæ contain normally less myeloïd than those of frogs. They were treated in the dark with osmic acid; a light-brown colour was produced which underwent no change in daylight, showing that the visual purple had been destroyed.

Potassium permanganate and iodine also destroy visual purple. Ferric chloric, potassium chlorate and iodate, and a solution of potassium chlorate, containing 2 per cent. of ammonium metavanadate, have no effect. These reactions show that visual purple is a substance already highly oxidised.

Visual purple was shown by Kühne to be soluble in solution of bile salts. This is because bile dissolves out from the rods a vehicle in which visual purple is soluble. This vehicle is probably a substance resembling myosin. Solutions of free toluylenediamine or of its neutral acetate break up the rods into cross discs, but do not dissolve out the purple from the fragments.

After a frog has been poisoned by pilocarpin, the regeneration of rhodopsin in the dark after exposure to light is hastened, not hindered, as Kühne and Ayres found in the rabbit. Atropine and muscarine have no such influence. The brightness of the sky, the body temperature of the frog, and the force of the blood circulation, are important factors in this regeneration, so that control experiments with unpoisoned frogs are always necessary.

Myeloïd is not lecithin as some have supposed. Lecithin is not coloured so intensely black by osmic acid as is myeloïd, nor is the coloration removed by hydrogen peroxide. Myeloïd is probably vitellin, which is a compound or very intimate mixture of globulin with lecithin; it is deeply blackened by osmic acid, and this colour is destroyed by hydrogen peroxide. Vitellin and myeloïd are also alike in being soluble in concentrated solutions of salts like ammonium chloride. On the other hand, vitellin is not decomposed by ether, and therefore after treatment by this reagent its behaviour to osmic

acid is unchanged. Myeloïd, however, is soluble in ether, this may be accounted for by the salts present in the lymph of the retina, or by the fact that the ether used was not free from alcohol. It is well known that the presence of certain salts modifies in a similar way the action of ether on egg albumin. The difference in the osmic acid colour produced in the rods and that in nerve-fibre, is probably due to the presence of neurine in the latter. W. D. H.

Intestinal Digestion of Albumin. By J. Wenz (*Zeit. Biol.*, **22**, 1—22).—Discrepancies in the results of previous observers on this subject are due to care not having been taken to prevent the admixture with the intestinal juice of other enzymes present in the alimentary canal, nor to prevent putrefaction, whilst the sense of smell was relied on as a test of putrefaction, without looking for bacteria. To this Masloff's work (*Unters. Physiol. Institut*, Heidelberg, 1878) is an exception, he employed thymol or salicylic acid as antiseptics, and found that the intestinal juice had no digestive power on fibrin.

In the present researches, care was taken to obviate both these sources of error, the first by the prolonged washing of the intestine with various agents, the second by the addition of a piece of thymol, or of a few drops of a 25 per cent. alcoholic solution of thymol in each experiment.

The enzymes hitherto known can be extracted and isolated by appropriate treatment with water, dilute acids, and alkalis, or glycerol, without any loss of their property of digesting albumin. Proceeding on this basis, tracts of intestine (of dogs and pigs) were first washed for a long time with water, till this fluid passed through perfectly clear, then opened on a glass plate, and the mucous membrane detached, washed thoroughly with alcohol and ether, dried and extracted with glycerol, water, 3 per cent. sodium chloride solution, 0·2—0·4 per cent. sodium hydroxide solution, and 1 per cent. salicylic acid.

In the case of two dogs, intestinal fistulæ were made by Thiry's (*Sitz. Wien. Akad.*, **50**) plan, namely, by the isolation of a loop of ileum by means of ligatures and the establishment of an external opening; the intestine included between the ligatures was daily washed out with saline solution for six days, and the secretion collected. In this way from 1 to 1·5 c.c. of juice was on the average collected from 30 cm. of intestine. It was transparent, yellowish, alkaline, became slightly cloudy on neutralisation, and contained no peptone.

The efficacy of the various extracts and of the juice was tried in neutral, acid, and alkaline solutions on the various kinds of albumose described by Kühne and Chittenden, namely, proto-, hetero-, deutero-, dys-, and anti-albumose, also on anti-albumate and anti-albumoid; these bodies being intermediate products in the conversion of native proteïd into peptones. The fluid was examined for peptone at intervals varying from 6 to 72 hours.

The method adopted for the detection of peptones was as follows: the fluid was saturated by shaking it well with ammonium sulphate. This salt precipitates all proteïd bodies but peptones. The filtrate was tested for peptone by the biuret reaction. It must be here stated

that Heynsius maintains that ammonium sulphate precipitates peptones also (*Pflüger's Archiv*, **34**). Kühne takes the opposite view, and explains Heynsius' results by saying that the commercial peptone used by Heynsius consists entirely of albumoses.

The following conclusion is drawn:—Intestinal juice of the dog and pig has no peptonising action on the decomposition products of albumin. In some exceptional cases a trace of peptone seems to be formed from deutero-albumose, the albumose most allied to peptone; this is possibly due to the fact that the saturation with ammonium sulphate had been incomplete, and that therefore some deutero-albumose (which gives the biuret reaction) was present in the filtrate.

W. D. H.

Proteïd Digestion. A. Stutzer (*Zeit. physiol. Chem.*, **10**, 153—162).—Kellner (Abstr., 1881, 296) found by experiments with 25 different diets on herbivorous animals, that Stutzer's method of estimating the digestibility of foods by the action of artificial gastric juice, gave results which were 0·4 per cent. of dry food material higher than those obtained in the living animal, whatever the diet. Pfeiffer (*J. Landwirthschaft*) obtained a similar result with omnivorous animals. That is an amount of nitrogen corresponding to 0·4 per cent. of the dried food passes off in all cases in the form of products of metabolism. The so-called depression of proteïd digestion by a diet poor in nitrogen therefore does not exist.

A method which may be employed to separate the substances containing nitrogen, which are products of metabolism, from other nitrogenous substances in the excrements, is to subject them to the action of artificial gastric juice; the former being soluble, the latter not. Any error from the presence of epithelial cells from the intestinal walls must be very small. The average of ten experiments gives the quantity of nitrogen in the fæces contained in products of metabolism as 0·4 per cent. of dry food material.

Digestion coefficients may be reckoned in three ways:—(*a.*) The difference between food-nitrogen and fæces-nitrogen, *plus* the nitrogen of the products of metabolism in the fæces (0·4 per cent.). (*b.*) The difference between food-nitrogen and that part of the fæces-nitrogen insoluble in gastric juice. (*c.*) The difference between the food-nitrogen and that part of the food-nitrogen insoluble in gastric and pancreatic juices.

In the ten experiments, these three methods gave results within a few decimal points of one another. W. D. H.

Nutritive Value of some Digestion Products of Albumin. By S. Pollitzer (*Pflüger's Archiv*, **37**, 301—313).—A dog was fed for successive periods on meat, peptone, protalbumose, heteroalbumose, and gelatin. The amount of nitrogen ingested per diem was approximately equal in all cases. The following table gives the results of the nitrogen estimations in food and excreta.

	Number of days.	Nitrogen per diem		
		In food.	In urine and fæces.	Gain or loss.
1. Meat	6	2·4 gram	1·9 gram	+ 0·5 grm.
2. Peptone	2	2·4 „	1·8 „	+ 0·6 „
3. Meat	3	2·4 „	1·9 „	+ 0·5 „
4. Protalbumose	2	2·4 „	1·8 „	+ 0·6 „
5. Heteroalbumose	1	2·5 „	1·7 „	+ 0·8 „
6. Meat	4	2·1 „	1·7 „	+ 0·4 „
7. Gelatin	3	2·3 „	2·8 „	− 0·5 „
8. Meat	4	2·1 „	1·7 „	+ 0·4 „

From this, the conclusion is drawn that peptone and hemialbumose have the same nutritive value as meat, this result contrasting with the loss of nitrogen (and body-weight) when gelatin is employed as a food. W. D. H.

Nutritive Value of the so-called Meat-peptones. By N. Zuntz (*Pflüger's Archiv*, **37**, 313—324).—Meat-peptones owe much of their value to the large amount of extractives and salts they contain; this paper deals only with their nitrogenous constituents. Such a research was necessary, since Kühne has recently shown that commercial peptones consist in large measure of albumoses.

Dogs were fed on meat, and then for successive periods on Kemmerich's and Koch's peptones, containing an equivalent amount of nitrogen. A certain constant amount of fat was mixed with the diet. The nitrogen in urine and fæces was analysed and the animals weighed. The animals take the artificial food with much aversion, on account of its bitter taste, so that it had to be administered by an œsophageal bougie. Often it caused vomiting and purging. While it composed their diet, they were in an emaciated and sick condition. This is borne out by the results of nitrogen estimation, as is shown in the following table:—

Diet.	Number of days.	Daily gain or loss of nitrogen.
Meat and fat	5	+ 0·2 gram
Kemmerich's peptone and fat	6	− 0·5 „
Meat and fat	5	+ 0·2 „
Koch's peptone and fat	4	− 0·5 „
Meat and fat	5	+ 0·3 „

After the animals had been fed for some days on a diet very poor in nitrogen, consisting of rice and fat, the addition of peptonised meat to this produced a gain in flesh for some days, and then the nitrogenous exchange and body-weight remained fairly constant.

E. Pfeiffer (*Berliner klin. Wochensch.*, 1885, **30**) concludes from clinical experience that Kemmerich's peptone is more nourishing

than Koch's. This is confirmed by analysis, which shows that the former contain 9·7 per cent., the latter 8·02 per cent. of nitrogen.

W. D. H.

Digestion of Various Foods in the Human Intestines. By H. Malfatti (*Bied. Centr.*, **15**, 40—41).—The author made certain experiments on himself in Voit's laboratory. For two days he ate daily maize flour, 540·8 grams dry substance, boiled with water containing a little salt, his drink being water. For another three days he used maize flour with butter; 667·5 grams dry substance and 80·1 gram butter. Another three days he ate cheese with the maize flour; 688·7 grams dry substance and 130 grams Swiss cheese. The following percentages of the constituents of these foods occur in the fæces :—

	Maize flour.	Maize and butter.	Maize with cheese.
Dry substance	6·30	7·96	4·20
Nitrogen	18·28	31·54	7·31
Fat	42·14	56·83	9·34
Carbohydrates	3·42	3·69	2·32
Ash	30·48	37·90	19·37

The effect of cheese on the digestion of the maize is surprising, and is of considerable interest when it is remembered that the food of the Tyrolese and North Italians consists largely of polenta and cheese. Further experiments were made with pease and meat; for two days pease, containing 957·9 grams dry substance, were taken with 151 grams butter; for another two days no butter, but pease containing 1004·2 dry substance; and in another three days pure flesh containing 581·03 grams dry substance; the percentages of the constituents remaining undigested in the fæces were as follows :—

	Pease and butter.	Pease alone.	Flesh.
Dry substance	8·69	9·86	2·77
Nitrogen	15·20	30·76	1·62
Fat	8·64	111·07	1·78
Carbohydrates	4·19	4·07	—
Ash	34·19	41·10	8·21

These results agree well with those of Rubner. J. F.

Digestion of "Saccharin." By A. Stutzer (*Bied. Centr.*, **15**, 64—65).—This substance was discovered by Fahlenberg and Remsen, and termed by them anhydro-orthosulphaminebenzoic acid (Abstr., 1879, 628); it forms white crystals, which are soluble with difficulty in cold, but easily in hot water, and is distinguished by its intensely sweet taste, with a slightly almond flavour, which is perceptible in a solution of 1 part in 10,000 of water.

The author's experiments with this substance were made to ascertain its effect on the digestion of protein substances; finely-ground cocoa cake as sold for fodder, bread and meat were submitted to the

action of the gastric juices, with the result of finding trifling effects, certainly none of a hurtful kind. The transformation of starch into sugar is hastened by the addition of "saccharin" to the malt solution, if sugar is also present; if sugar is absent, the diastatic action is retarded. The addition of 0·01 to 0·1 gram of "saccharin" to the food of rabbits and dogs caused no injurious results. In order to test its power of retarding decomposition, a dilute extract of peptonised meat was prepared; its action was feeble, and when used for arresting decay, salicylic acid should always be added. With dilute solutions of starch and cane-sugar, it acted almost as well as thymol and salicylic acid.

The author believes that the substance will be used in future, instead of cane-sugar, to sweeten pastry, liqueurs, medicines, &c.

J. F.

Note.—The name saccharin ought not to be applied to this substance, having been in use since 1880 to designate the carbohydrate originally obtained by Peligot by the action of lime on cane-sugar.—A. J. G.

Digestion Experiments. By H. P. Armsby (*Amer. J. Sci.*, 1885, 355—369).—Sheep were fed with clover-hay, cotton-seed meal, and malt coombs. The following table shows the average percentage of the food that was digested:—

	Dry matter.	Organic matter.	Protein.	Albuminoïds.	Fibre.	Nitrogen-free extract.	Fat.
Clover-hay	51·8	52·7	49·4	36·5	47·7	57·7	42·7
Cotton-seed....	81·1	80·7	88·7	87·7	—	67·8	103·2
Malt coombs ..	67·1	67·2	80·2	71·2	32·9	68·1	104·6

After giving full details of his experiments, the author proceeds to discuss the question of the errors of the results as occasioned by errors in weighing out the food, and analytical errors, &c. For the hay (alone) experiments, it is computed that the figures representing digestion given above are subject to the following errors:—Dry matter $\pm$ 0·08 per cent., protein (N $\times$ 6·25) $\pm$ 1·15, and crude fibre $\pm$ 0·62. But the errors in the experiments with the bye-fodders are increased by the phenomenon which Fischer has observed, that the digestibility of the same fodder by the same animal may vary at different times. Combining all the possible errors, we find—

	Malt coombs.	Cotton-seed meal.
Dry matter	4·25 per cent.	4·74
Protein	5·66 ,,	3·17
Crude fibre	10·91 ,,	52·37

It was evident that the fat determinations were valueless, so that on the whole the results arrived at have but little scientific value.

Conceding this, the question then arises as to the value of all other digestive experiments. There can be no doubt, however, that they possess a certain practical value, but none of the results can properly enter into any scientific calculation. E. W. P.

Exchange of Material in the Pig. By E. Meissl (*Zeit. Biol.*, **22**, 63—160).—These experiments on the pig were undertaken in consequence of the value of this animal from a commercial point of view.

Various diets were tried, full, medium, and scanty; they consisted chiefly of rice and barley. The animals used were of the Hungarian and Yorkshire breeds, but the results in the two agree closely.

Full analyses are given of the fodder used, and also of the various egesta by the lungs, rectum, and kidneys in each case for the period of a week. Analyses are also given of the excreta during inanition.

The results are interesting to the chemist and physiologist, as showing among other things the possibility of fat being formed both from albuminous and carbohydrate food. W. D. H.

Formation of Trypsin. S. Levascheff (*Pflüger's Archiv*, **37**, 32—44).—Trypsin does not exist as such in the pancreas, but a precursor of the ferment or zymogen is present in the cells of that organ. Heidenhain showed that a glycerol extract of a fresh pancreas is inactive, but after it has stood 24 hours or been treated with 1 per cent. acetic acid, glycerol will extract an active ferment.

These generally accepted facts having been rather shaken by some experiments of Weiss (*Virchow's Archiv*, **68**, 413), this research was undertaken, and the results confirm those of Heidenhain. The extracts were in all cases made with concentrated glycerol.

By placing a cannula in the pancreatic duct, it was found in the dog that subcutaneous injection of pilocarpin increased not only the salivary, but also the pancreatic secretion. The increase in secretion followed the injection in the course of a minute. The pancreas in dogs poisoned by pilocarpin, yielded no trypsin to glycerol, even after the lapse of 24 hours, all the zymogen having been converted into trypsin, and discharged into the intestine previous to death.

In animals from whom food had been withheld for 24 hours, the yield of trypsin was very abundant; that is, if the extract was made 24 hours after the death of the animal. In animals from whom food had been withheld for a longer time, glycerol extracted no trypsin 24 hours after death; that is, the zymogen had disappeared. Microscopic examination of these glands showed the unexpected result that the cells were filled with the granules with which the zymogen has been hitherto identified. The conclusion is drawn that these granules are not themselves the zymogen, but only carriers of it—a conclusion to which Heidenhain subscribes in a footnote. The opposite condition, zymogen without granules, has not been observed.

W. D. H.

Fate of Pepsin and Trypsin. By H. Leo (*Pflüger's Archiv*, **37**, 223—231).—Several observers have found pepsin in the urine, blood, and various organs of the body. Sahli (*Pflüger's Archiv*, **36**, 209)

describes both pepsin and trypsin in the urine. The pepsin found in other organs than the stomach is probably not formed in them, as it would be useless there owing to the alkaline reaction of those parts, but probably in all cases comes from the stomach.

Small pieces of fibrin soaked in the urine absorb the pepsin therefrom; on removing them to 0·1 per cent. hydrochloric acid they are rapidly digested. If the fibrin, however, has been preserved for a long time under alcohol this does not occur. The pepsin which is thus shown to be present is not derived from the blood, which yields the fibrin, as is shown by control experiments in which the fibrin was not first soaked in urine. If the urine is first boiled, the activity of the pepsin in it is destroyed, and digestion of fibrin does not occur. Pepsin was thus shown to be present in the urine of 60 healthy persons. Morning urine is richest in pepsin. In cancer of the stomach and typhoid fever, the urine contains no pepsin.

Trypsin is absent in the urine of healthy and sick people. Sahli's results are explained by putrefaction not having been prevented in his experiments. A few drops of alcoholic solution of thymol will prevent putrefaction, and then digestion of the fibrin never occurs in a solution of 1 per cent. sodium carbonate.

The question then arises, is trypsin destroyed in the alimentary canal, or in the way thence to the kidneys? Fresh fæces were found to contain no trypsin. It is unlikely for it to escape unchanged from the alimentary canal, because its presence in the lymph, or blood would cause digestion of the protoplasmic elements with which those fluids come in contact. Moreover, it has never been found in the blood or tissues, hence it must be destroyed in the alimentary canal itself. By making extracts of different parts of the intestines of one dog, the probable conclusion is drawn that pepsin disappears in the second third of the small intestine, and trypsin in the lower third.

W. D. H.

Conversion of Peptone by the Liver. By J. Seegen (*Pflüger's Archiv*, **37**, 325—341).—From previous observations (*ibid.*, **28**), the author concluded that the liver possessed the power of converting peptone into sugar and some new nitrogenous substance or substances. An increase of sugar takes place either when peptone is given as food, injected into the portal vein, or placed in contact with pieces of excised liver in defibrinated blood; it was anticipated that an increase of the crystalline nitrogenous decomposition products would occur. Owing to the normal percentage of these products in the liver varying within such wide limits, even in the same species of animal, it was only possible to obtain any conclusion by making comparative experiments on parts of the same liver. A full description of the methods is given. The results of six experiments show a marked increase in the decomposition products, as anticipated. The author replies at length to Hoffmeister's criticism (*Arch. Pharm.*, **19**, 1—2) of his former paper. J. P. L.

Sugar in the Blood with Reference to Nutrition. By J. Seegen (*Pflüger's Archiv*, **37**, 348—368).—In an earlier investigation, the author has shown that the percentage of sugar in an excised liver can

increase from 0·4 per cent. to 3·0 per cent., without any alteration in the quantity of glycogen, and still more recently that this increase is probably due to the decomposition of peptone. In the present experiments, he has determined the influence of inanition and various carbohydrate diets on the formation of sugar in the liver. The experiments were all made on living animals. The amount of sugar formed in the liver was calculated from the difference between the percentage of sugar in the blood of the portal and hepatic veins. The blood of the hepatic vein is *always* much richer in sugar than the blood of the portal vein, even during long periods of inanition, although the quantity of sugar formed in a single day exceeded the total amount of glycogen present in the body.

If Bernard's explanation of the formation of sugar were correct, the percentage of sugar in the portal and hepatic veins ought to be exactly the same with a carbohydrate diet. He concludes, therefore, that glycogen does not furnish the sugar, but fulfils some other, at present unknown, metabolic function. J. P. L.

Non-fermentable Reducing Substances in Blood. By J. Seegen (*Pflüger's Archiv*, **37**, 369—374).—The author considers the lower percentage of sugar found in blood by fermentation to be due solely to incomplete fermentation, and not, as stated by Otto, to the presence of non-fermentable reducing substances. J. P. L.

Glycogen in Ciliated Infusoriæ. By E. Maupas (*Compt. rend.*, **101**, 1504—1506).—*Paramecium aurelia*, which was taken as a type of the ciliated infusoriæ, contains a substance which is quite distinct from the solid granulations of the gregarinæ, and is identical with the glycogen from the liver of a rabbit in its behaviour towards alcohol or iodine solution under the microscope.

In one instance of a rich cultivation of *P. aurelia* no glycogen could be detected. C. H. B.

Amylaceous Granules in Gregarinæ. By E. Maupas (*Compt. rend.*, **102**, 120—123).—These granules exist in all gregarinæ, without exception, and also in certain parasitic ciliated infusoriæ. They vary in size and shape, occurring in flattened ovals, spheres, discs, and more or less irregular forms. They are coloured yellowish-brown by iodine, and under the microscope show a concentric structure, and a black cross with polarised light. The granules are insoluble in cold water, but dissolve in water at 45—60°, and the solution is coloured violet by iodine, and reduces Fehling's solution. The granules are distinctly amylaceous in character, and in some of their properties are identical with the starch of the floridæ. The author adopts the name *zooamylum*, proposed by Bütschli. C. H. B.

Presence of Sugar in Urine on a Diet of Cane-sugar. By J. Seegen (*Pflüger's Archiv*, **37**, 342—347).—During an exclusively sugar diet, a small percentage of both unchanged cane-sugar and invert-sugar is excreted. J. P. L.

Occurrence of Volatile Fatty Acids in Urine. By R. v. Jaksch (*Chem. Centr.*, 1885, 905).—The author finds traces of fatty acids in normal human urine; the amount does not exceed 0·008 gram per diem. By oxidising normal urine, formic, acetic, and probably butyric acids are formed to the extent of 0·9—1·5 gram in the diurnal quantity. Under certain pathological conditions, the proportion of free acid is increased, but not that obtained by oxidation. In cases of fever and liver disease, from 0·6—1 gram of free acid, chiefly acetic, was found.

W. R. D.

Phosphatic Urines, supposed to be Albuminous. By P. Carles (*J. Pharm.* [5], **13**, 49—50).—When a urine is heated to ascertain the presence or otherwise of albumin, it frequently happens that a sensible turbidity is produced in the absence of all proteïd substances. If the urine is very acid, this misleading appearance is never obtained; but it always occurs if the liquid be only faintly acid or neutral. If a recent urine is acid, the earthy phosphates occur in it in the monobasic condition, that is to say, stable towards heat; but when, in consequence of ammoniacal fermentation, this acidity diminishes, the phosphates pass into the bibasic state, yet are still soluble and without effect on the limpidity of the liquid. But when the urine becomes alkaline, the phosphates become tribasic and are spontaneously deposited. Now in the state of bibasic phosphate, the calcium salt is very unstable, and on heating to a point even below 100°, it is dissociated into soluble monocalcium phosphate and tricalcium phosphate, which is precipitated and may be mistaken for coagulated albumin.

J. T.

Aromatic Compounds in Urine and Putrefaction in the Intestines. By E. Baumann (*Zeit. physiol. Chem.*, **10**, 123—133).—The following conclusions are arrived at:—In addition to the seven ethereal hydrogen sulphates in the urine hitherto described, others of the same category occur normally; nothing further can be at present stated as to their composition. They can be shown to exist in the urine of horses and dogs after the separation of the other ethereal hydrogen sulphates.

All these compounds in urine are derived from putrefactive processes in the alimentary canal. If these be stopped by inanition *plus* the administration of calomel in dogs, the ethereal hydrogen sulphates are absent in the urine. Confirmation of this was found in a patient who had a fistula in the upper part of the intestine, and whose intestine below this was functionless; putrefactive processes did not occur, and these acid salts were absent from the urine.

The aromatic hydroxy-acids, hydroparacoumaric acid and parhydroxyphenylacetic acid, or perhaps only the latter, are found by similar observations not to be wholly dependent on putrefactive processes, but are also formed in the tissues.

The hippuric acid contained in the urine of flesh-eating animals is derived exclusively from putrefaction in the intestines.

Cynurenic acid, which is a decomposition-product of proteïds, and found hitherto only in dog's urine, occurs independently of putrefaction in the alimentary canal.

W. D. H.

Chemical Composition of Nerve Substance. By J. Chevalier (*Zeit. physiol. Chem.*, **10**, 97—105).—The human sciatic nerve was employed, and by means of the usual methods employed for estimating the substances mentioned below, the following was found to be the percentage composition of dry white nerve substance :—

Cerebrin	11·30
Lecithin	32·57
Cholesterin	12·22
Proteïd	36·80
Neurilemma and other substances soluble in soda	4·04
Neurokeratin	3·07

The fat found to be present in nerve is probably contained in the connective tissue between the nerve fibres. Whether this is really the case can be settled by an analysis of white brain matter, which the authoress intends to undertake. W. D. H.

Toxic Action of Alkaline Salts. By C. Richet (*Compt. rend.*, **102**, 57—60).—The author has extended his researches (*Compt. rend.*, 1885) to the action of the iodides and bromides of potassium, lithium, and rubidium on pigeons, fishes, and guinea-pigs, and arrives at the following general conclusions :—Amongst chemically analogous substances like the alkaline salts, the maximum fatal dose is sensibly proportional to the molecular weight; in absolute weight, the metals are more poisonous the higher the molecular weight; in equal molecules, the metal with the highest atomic weight is the most poisonous; in absolute weight, the chlorides are more poisonous than the bromides, and the bromides than the iodides, but in equal molecules the order is reversed. The differences observed between the three metals are not very great.

The poisonous effect on pigeons is much greater at a low temperature, but the minimum fatal dose for fishes is not materially affected by the temperature. C. H. B.

Physiological Action of Lithium, Potassium, and Rubidium Salts. By J. Blake (*Compt. rend.*, **102**, 128—129).—The author claims priority for his investigations of the poisonous action of salts of the alkali metals. His results showed that potassium salts kill by paralysing the action of the heart, whilst lithium and rubidium salts arrest the pulmonary circulation. The fatal dose of each metal per kilo. of body-weight, when injected into the veins in the form of a salt, is lithium 0·19, rubidium 0·087, and potassium 0·047.

C. H. B.

Physiological Action of Acetophenone. By A. Mairet and Combemale (*Compt. rend.*, **101**, 1506—1507; and **102**, 178—181).—Experiments were made on dogs, cats, rabbits, guinea-pigs, and sane and insane human beings, the acetophenone being administered in several different ways. Acetophenone is not a hypnotic, and its advantages as a sedative are very doubtful. It acts on the nervous

system and also produces congestive and inflammatory lesions of the kidneys, lungs, and liver. C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

Determination of Diastatic Activity. By C. J. Lintner (*Bied. Centr.*, 1885, 855—858).—Founding his method on Kjeldahl's researches, Lintner prepared his solutions as follows:—2 grams of air-dry starch is mixed with 60 c.c. of water and 10 c.c. of $\frac{1}{10}$ per cent. hydrochloric acid in a closed flask, and heated on a water-bath for 30 minutes. The starch, after that time has elapsed, is dissolved, and the quantity of liquid is made up to 100 c.c., after neutralising with soda. The malt solution is prepared from 25 grams of malt extracted with 500 c.c. water for six hours; this, according to Kjeldahl, is sufficient time to remove all diastase. For the estimation of the diastase in this extract, 10 c.c. of the starch solution is poured into 10 test-tubes, and to each test-tube with its contents is added 0·1, 0·2, 0·3, &c., c.c. of the malt extract; then each tube is well shaken and allowed to stand for one hour at 17°; after that time has elapsed, 5 c.c. of Fehling's solution is added, and the whole is heated in boiling water for 10 minutes. It is evident that the amount of diastase present in the malt is discovered by observation of two contiguous test-tubes, the one of which is blue, the other red.

E. W. P.

Action of Salicylic Acid on Ferments. By A. B. Griffiths (*Chem. News*, **53**, 28—29).—A solution containing 0·2 gram of salicylic acid per 1000 c.c. of water has been observed to destroy very quickly *Mycoderma aceti*, *Bacterium lactis*, and the butyric bacillus. It appears to act on and dissolve the cell-walls of these organisms, as also of dead torulæ; although living torulæ are not acted on, nevertheless their activity is impeded by the salicylic acid. Thus neither yeast nor saliva exert their fermentative faculties in the presence of this solution of salicylic acid. The yeast can, however, be revivified by treatment with sodium phosphate and potassium nitrate. Hence "diseased yeast" may be advantageously treated with such a solution of salicylic acid which is far below the poisonous strength.

D. A. L.

The Ammoniacal Ferment. By A. Ladureau (*Ann. Agronom.*, **11**, 522—525).—As a sequel to his previous researches (Abstr., 1885, 181), the author has endeavoured to find some substance, useful or at any rate innocuous to plants, with which to arrest the ammoniacal fermentation of urea, and so preserve farmyard manure from loss of ammoniacal nitrogen. A 2 per cent. solution of urea was fertilised with a little garden soil, and the following reagents were added:—

Phosphoric acid.—2 per cent. and 4 per cent. only partially arrested the formation of ammonia; smaller quantities had little effect.

Superphosphate of lime had no effect in quantities up to 4 per cent.

Ferrous sulphate had no effect in quantities up to 1 per cent.

Phenol.—0·5 per cent. only partially prevented the formation of ammonia. Smaller quantities had little or no effect.

Quicklime.—Even 1 per cent. exercised but little retarding action.

Sulphuric acid.—The addition of 1 per cent. had no effect.

Boric acid in the proportion of 0·4 per cent. only partially prevented the formation of ammonia. Smaller quantities were almost without action. J. M. H. M.

Influence of Light on the Growth of Yeast. By M. Key (*Bied. Centr.*, **15**, 71—72).—The development of yeast proceeds equally well whether exposed to light or in darkness. A nutritive solution was prepared, containing in a litre 100 grams of sugar, 2·5 grams of asparagine with 20 c.c. of a solution of mineral salts; equal portions were placed under two bell-glasses, one black and the other clear, and exposed to a strong gaslight, the heat from which was absorbed by a layer of water, so that the temperature was the same in both; the number of cells at the beginning and end of the experiment was counted. Of eight experiments, three gave an excess in the dark glass, five in the illuminated. J. F.

Activity of Chlorophyll under the Influence of the Ultra-violet Rays. By G. Bonnier and L. Mangin (*Compt. rend.*, **102**, 123—126).—Any action of the chlorophyll taking place when a plant is exposed to the ultra-violet rays will be masked by the process of respiration, which is especially active when exposed to these rays. The authors have shown, however, that the ratio $\frac{CO_2}{O}$ is independent of the nature of the rays impinging on the plant, and will remain invariable if respiration alone takes place. If, however, the chlorophyll becomes active, this ratio will be considerably modified; it will increase and may even exceed unity. The authors find that when plants are placed in the ultra-violet rays, the ratio $\frac{CO_2}{O}$ does materially increase, and hence they conclude that the invisible rays in the ultra-violet excite the activity of chlorophyll. C. H. B.

Asparagine in Hops. By H. Bungener (*Bied. Centr.*, 1885, 861).—The author has found that as much as 30 per cent. of the total soluble nitrogen in hops occurs as asparagine. E. W. P.

Occurrence of Coniferin and Vanillin in Asparagus. By E. O. v. Lippmann (*Ber.*, **18**, 3335—3336).—A considerable amount of coniferin, together with some vanillin, was obtained from the sap and cellular tissues of asparagus by the same method as that used by the author for separating these substances from beetroot-sugar. The distribution of coniferin and vanillin in vegetables is probably far more general than hitherto supposed. N. H. M.

Raspberry Juice. By A. Pabst (*Bull. Soc. Chim.*, **44**, 363—366).—The juice of the raspberry, after the pectous matters have been

removed, contains 99·5 grams of solids per litre, which yield 3·9 grams of an alkaline ash. The acidity of the juice is equivalent to 13·7 grams of sulphuric acid per litre, and is due partially to malic, but chiefly to citric acid; about 46 grams of lævulose and 25 grams of glucose are present. The red colouring matter present in the juice is soluble in water or alcohol, but is insoluble in ether: it seems to consist of two colouring matters; their aqueous solution becomes of a more yellowish tint on adding concentrated acids, the colour being restored on dilution. Alkalis, their carbonates, and carbonates of the alkaline earths change the colour to violet, and then to blue, whilst an excess of potash changes it to green; these alkaline solutions become brown on exposure to air. Oxidising agents, such as barium or hydrogen peroxide, first colour the solution yellow, and finally bleach it. The absorption spectrum of the colouring matter is described.

A. P.

Coca Leaves and Cocaïne. By Bignon (*Pharm. J. Trans.* [3], **16**, 265—266).—Coca leaves are neither nutritive nor tonic, when fresh they contain one alkaloïd only, *cocaïne*, and that as an inert salt. Fresh leaves, or leaves properly and freshly dried, yield 8 grams of cocaïne per kilogram. The Indians mix the leaves with lime and ashes before chewing, and thus liberate the alkaloïd. When the leaves are exhausted of cocaïne and distilled with alkalis *hygrine* is produced. Leaves packed damp undergo fermentation, and the cocaïne is then destroyed. Cocaïne is easily decomposed; even in solutions which are not absolutely neutral, incipient decomposition sets in. The anæsthetic properties are more powerful in the free alkaloïd than in its salts. The irritation caused by the use of cocaïne is here attributed to the cocaïne and not to the very minute quantity of hygrine present. Cocaïne is also said to be the cause of the dilatation of the pupil of the eye. Doses of 1 or 2 centigrams per day are regarded as illusory, 10 centigrams being an average dose.

D. A. L.

Analyses of Chicory-root. By A. Mayer (*Bied. Centr.*, 1885, 828).—Three samples of Dutch roots contained the following substances in parts per 100:—

Water	72·00—77·3
Albuminoïds	1·1
Fat	0·2
Inulin and other non-nitrogenous matters insoluble in alcohol	12·00—17·3
Crude fibre	1·40— 1·8
Sugar, &c.	5·60— 6·0
Bitter extract	0·05— 0·15
Ash	1·40— 1·9

The bitter compounds extracted by chloroform are soluble in water and alcohol, but insoluble in ether, they are precipitated by tannin or lead acetate, but are absorbed by bone charcoal; they are decomposed by sulphuric acid, but do not then yield any substance capable of reducing Fehling's solution.

E. W. P.

Mahwa Flowers. By A. H. Church (*Nature*, **33**, 343—344).—It having recently been stated that "Mahwa flowers" (the corollas of *Bassia latifolia*, a tree common in many parts of India, especially in Central Hindustan) form a cheap source of cane-sugar, a sample of these flowers from the Kew Museum, in their air-dried condition, was analysed with the following results:—

Cane-sugar	3·2
Invert sugar	52·6
Other matters soluble in water	7·2
Cellulose	2·4
Albuminoïds	2·2
Ash	4·8
Water at 100°	15·0
Undetermined	12·6

It is not at all probable that these flowers could have contained any large amount of cane-sugar when in the fresh condition (compare Riche and Remont, Abstr., 1880, 519). A. J. G.

Potassium Chloride as a Plant Poison. Essential Elements of Plants. By J. M. H. Munro (*Chem. News*, **53**, 2—3).—The author criticises rather severely the article "The Essential Elements of Plants," by Jamieson (*ibid.*, **52**, 257), both with regard to the statement that certain experiments foreshadow "the exclusion of sulphur, magnesium, and calcium from the list of plant essentials," and other points. Whilst admitting the interest attached to the fact that potassium chloride occasionally acts injuriously on plants, having confirmatory evidence in his own experiments, quoted below, he entirely disagrees with Jamieson's explanation, namely, that the poisonous action is due to the liberation of chlorine and free acid in the plant. In certain experiments made by the author with potatoes, receiving different manures, each manure being applied to 39 sets, and each set receiving the quantity indicated below, the cultivation being otherwise identical, the following results were obtained:—3 ozs. Peruvian guano (per set) gave 114 lbs. tubers (average of 5 rows); 2 ozs. cod-fish guano (containing 12 to 20 per cent. potash chiefly or partly as chloride) and potash, produced healthy plants and gave 102 lbs. of tubers; 1 oz. herring-fish guano (containing 12 to 20 per cent. potash chiefly or partly as chloride) and potash, 84 lbs. tubers; 8 ozs. dry Coventry sewage sludge, 86 lbs. tubers; 2 ozs. "ferrous superphosphate" (a mixture of calcium sulphate, monocalcium phosphate and ferrous sulphate about 12 per cent.), 82 lbs. tubers; 4 ozs. dried Coventry sludge, 76 lbs. of tubers; 8 ozs. "native guano," 74 lbs. tubers; 1 oz. cod-fish guano and potash, 72 lbs. tubers; 39 sets unmanured gave (average of 4 rows) 64 lbs. of tubers; whilst 39 sets, each manured with 2 ozs. dried Coventry sludge containing 20 per cent. of added potassium chloride, gave no tubers. Only a few plants appeared above ground, and they eventually died. The good result with ferrous sulphate was not unexpected, but the irregular action of the potassium chloride is not understood. D. A. L.

Glutinous Rice (Oryza Glutinosa, Loureiro). By U. Kreusler and F. W. Dafert (*Ann. Agronom.*, **11**, 478—480).—This variety of rice, which comes from Siam, is distinguished by giving a red-brown instead of a blue coloration, with iodine. It contains 86·72 per cent. dry matter, 100 parts of which are composed of—fat, 0·68; albuminoïds, 8·89; crude fibre, 0·76; sugar, 8·65: dextrin, 3·35; ash, 0·69; starch, 76·98. The starch appears to be identical with ordinary starch, except as regards its coloration by iodine; the brown or red colour was produced even when all the dextrin and sugar were washed away from the sample by cold water, and was visible in each starch granule under the microscope. It is not the result of any preparation or cooking of the rice grains. J. M. H. M.

Nourishment of Fruit Trees. By F. Tschaplowitz (*Bied. Centr.*, 1885, 845—848).—Young crab-apple trees were planted in a glass vessel filled with clay loam, and manured with calcium nitrate and phosphate, magnesium sulphate and potassium nitrate; the trees were divided into groups, and to each group a different amount of the above mixture was given; in a second series, the above conditions remained the same, except that the soil was previously freed from clay; in a third series, trees growing *in situ* received the nutrient solution, and in a fourth series the trees, after washing, were grown in the solution itself, to which ferric phosphate had been added. As regards this last series, it was noted that only those trees growing in a dilute solution, 0·1 per cent., flourished, for when the solution was stronger, 0·5 per cent., spots appeared on the leaves. As was to be expected, the plants belonging to series I, which received the greatest amount of solution, 5 grams, flourished most, the rest soon died. The plants growing in the washed soil grew better than those in the unwashed earth, and nothing specially noticeable was observed concerning the third series. The author thinks that it would have been better to have given the manure at a later period of the year, in July. Other experiments were afterwards instituted, when it was noticed that superphosphate darkened the colour of the leaves, increased their number and size, and lengthened the shoots. The same phenomena were noticed when ammonium sulphate was employed, and the usual results of manuring with saltpetre were noticed, whilst potassium sulphate produced but little effect. E. W. P.

Cultivation of Potatoes. By F. Janowsky (*Bied. Centr.*, 1885, 836—840).—The first part of this article is of purely agricultural interest; in the second part the yield of 53 varieties of seed cultivated under the same conditions is shown. Finally, it is stated that kainite forces the growth, but then the haulms are pale and weak. The percentage of starch in the 53 varieties varied greatly, the lowest percentage being 11·5, whilst the highest was 20·5 (Climax).
E. W. P.

Preservation of Stable Manure. By Hickethier and Holdefleiss (*Bied. Centr.*, **15**, 24—27).—Four heaps of fresh cow manure were prepared, so that no rain but that falling perpendicularly could reach it; one heap was left so, the second mixed with a weighed

quantity of kainite, the third with phosphatic gypsum, the fourth covered with humous earth. After being left thus for seven months, it was found that three, Nos. 1, 3, and 4, were fairly decomposed, the other, No. 2, was as fresh as if it only had lain a few weeks. From the analyses of the manures when fresh, and at the end of the experiment, the authors found that the loss of organic matter in the three samples amounted to about one-third of the dry weight, the gypsum prevented the loss slightly, the kainite on the contrary caused the loss to be very small; the mixture with kainite, however, would take longer time to produce effects than would that already decomposed. The proper mixing of the preservative is difficult on farms, leading to a considerable loss of ammonia, the author estimating it at 30·5 German pounds per head of cattle per annum. J. F.

Manuring Oats with Thomas Slag. By H. Bieler, Jun. (*Bied. Centr.*, **15**, 29—30).—This paper is a record of further experiments on the utilisation in agriculture of this bye-product. With nitrate of soda, it yields good results, but succeeds better when mixed with both that substance and kainite; by a judicious mixture of materials, the author thinks the slag will be an economical manure, but recommends it to be sown as early in the season as possible (comp. Fleischer, this vol., p. 277). J. F.

Analytical Chemistry.

Supposed Error in Working with the Nitrometer. By G. Lunge (*Ber.*, **19**, 111—112).—In reply to Bayley (*Chem. News*, 1886, 6), the author maintains his previous statement (Abstr., 1885, 954), that no appreciable quantity of nitric oxide remains dissolved by the sulphuric acid in the nitrometer. Bayley's results are probably due to his not having taken sufficient care that the drop of acid in the narrow part of the tube immediately under the stopcock should be brought in contact with the mercury. The author has made a slight alteration in his nitrometer to render such an error less possible.

L. T. T.

New Applications of the Nitrometer. By G. Lunge (*Chem. Ind.*, 1885, 161—171).—Allen has described (*J. Soc. Chem. Ind.*, 1885, 178) various ways in which this instrument can be used for technical analysis. These can be still further extended. Used as an *absorptiometer*, the diminution in the gas volume can be read off, or by the side tube of the three-way cock the liquid can, without contact with air, be expelled for analysis.

Calculation can be simplified in the reduction of gas volumes to normal temperature and pressure, by using a nitrometer in which 100 c.c. (at 0° and 760 mm.) of moist air are permanently confined. Correction for tension of aqueous vapour is made by raising the mercury level in the open tube to a height above that in the closed

one equal to the tension at the existing temperature. In reducing the volume of a gas obtained in an analysis, this instrument is read simultaneously and its reading used as a divisor.

When estimating ethyl nitrite by Dott's reaction, Allen fills the nitrometer with brine. This may also be done in the determination of urea by hypobromite, but it is better to fill with mercury, and use a flask connected by rubber tube to the nose of the three-way cock for the reaction. As the flask can be heated it admits of the determination of ammonia (by hypobromite), of carbonic acid, and therefore of acids, alkalis, manganese oxides, &c. Tables by Dietrich (*Zeit. anal. Chem., passim*) give the most complete account of the necessary corrections.

The action of peroxide of hydrogen on acidified permanganate, which serves for the determination of the active oxygen of either reagent when the other is in excess, takes place also with chloride of lime in the absence of acids, and with potassium ferricyanide in alkaline solutions. Half the oxygen evolved comes in each case from the hydrogen peroxide. M. J. S.

Detection of Nitrates and Chlorates. By A. Béhal (*J. Pharm.* [5], **12**, 490—492).—The reaction is based on the property possessed by nascent hydrogen of reducing nitrates to ammonia and chlorates to chlorides. The solution to be tested is boiled with double its volume of potash solution (46° Baumé), until the absence of ammonia in the vapour is assured, as shown by litmus-paper. A fragment of metallic zinc is added to the liquid and a drop of copper sulphate solution; if on boiling 5—6 minutes reddened litmus becomes blue in the vapour evolved, the presence of a nitrate is indicated. If the original solution contained no acids precipitable by silver nitrate after strongly acidifying with nitric acid, a portion of the liquid which has been boiled with zinc is decanted, strongly acidified with nitric acid, and treated with silver nitrate, a white precipitate indicates the presence of chlorate in the original solution. If ammonia compounds are present in the original solution, a larger quantity of potash is employed. If acids precipitable by silver nitrate in nitric acid solution are present, they are removed by means of that precipitant before testing. No account is here taken of other oxygenated compounds of nitrogen, nor of other oxygenated compounds of chlorine, nor of those of bromine. If the last is in question, the silver salt obtained is further examined by the ordinary method. J. T.

Phosphoric Acid soluble in the Soil. By A. Thomson (*Chem. Ind.*, 1885, 205—206).—The ammonium citrate method of determining "reverted" phosphoric acid does not give concordant results. On the other hand, "solubility" in the ordinary sense is not required in manurial phosphates. It is only valuable as causing a minute subdivision and wide diffusion of the particles of calcium phosphate. The author expresses his concurrence in the views of Stutzer (*Chem. Ind.*, Feb., 1884), and gives the results of the examination for soil-solubility (Bodenlöslichkeit) of numerous phosphatic manures by the citric acid extraction method (Abstr., 48, 439). M. J. S.

Separation of Arsenic from the Alkaline Earths. By L. W. McCay (*Chem. News*, **53**, 39—40).—The solution slightly acidified with nitric acid and heated to boiling, is mixed with excess of silver nitrate, and then made slightly alkaline by the gradual addition of dilute ammonia, stirring vigorously. When cool, the liquid is filtered, and the silver determined in it by Volhard's method, or the silver arsenate re-dissolved in ammonia, the solution evaporated and the residue weighed. Good results are obtained and are not affected by the presence of small quantities of ferric and aluminium oxides.

D. A. L.

Precipitation and Estimation of Manganese and Iron indirectly by means of Hydrogen Peroxide. By J. J. Barlow (*Chem. News*, **53**, 41—42). — The following modification in the analytical examination of the metals of the iron-group is suggested. The filtrate from the precipitate obtained on adding ammonium chloride and ammonia is warmed, treated with excess of ammonia, and then drop by drop with hydrogen peroxide, which under these circumstances precipitates the manganese only, the whole mass is then boiled and filtered. In this way the manganese can be completely and quantitatively separated with facility.

When iron is present as well as manganese, but chromium and aluminium are absent, the solution is mixed with ammonium chloride and ammonia, boiled and precipitated with hydrogen peroxide. The mixed manganese and iron oxides are weighed, distilled with hydrochloric acid, the chlorine evolved estimated by absorption in a solution of potassium iodide, &c. From this the quantity of manganese present and, by difference, that of the iron may be calculated.

D. A. L.

Determination of Iron and Aluminium in Phosphates. By M. Kretschmar (*Chem. Centr.*, 1885, 952).—After purifying by precipitation, the phosphoric acid is determined in the precipitate of iron and aluminium phosphate by the "molybdate" method. The iron and aluminium are found by difference. W. R. D.

Quantitative Determination of Niobium. By T. B. Osborne (*Amer. J. Sci.*, **30**, 329—337).—Niobium occurs in nature almost always in association with tantalum and titanium, in the presence of which it has been hitherto impossible to obtain more than an approximate determination.

In order to analyse a mineral containing the three elements, the mixed oxides can be obtained in the usual manner by fusing the finely ground mineral with potassium pyrosulphate, digesting with water, filtering, heating the residue with ammonium sulphide, washing to remove tin and tungsten if present, treating the residue with dilute sulphuric acid to remove iron, washing, and igniting with ammonium carbonate. After obtaining the combined weights of the oxides, fuse with potassium pyrosulphate, digest with water, and dissolve the residue in hot hydrofluoric acid, evaporating nearly to dryness on the water-bath. Dissolve the fluorides thus obtained in concentrated hydrochloric acid, then add amalgamated zinc and a piece of platinum, and allow the solution to reduce in a stream of

carbonic acid for 45 minutes at a temperature of 80°. After cooling, pour the reduced solution into a beaker and dilute with distilled water to 350 c.c.; then add a standard solution of potassium permanganate until the solution becomes perfectly clear. Add ammonia in slight excess, then sulphuric acid, thus obtaining a solution containing a very small amount of free acid and practically free from fluorides. Dilute the solution to 500 c.c., and bring 50 c.c. into a Nessler tube, and add 2 c.c. of hydrogen dioxide. To another tube add about 40 c.c. of water and 2 c.c. of hydrogen dioxide. A standard solution of titanic acid is then run in until the colour in the two tubes is alike. The number of c.c. of the standard solution multiplied by 10 gives the number of milligrms of TiO_2 in the solution. By calculating the amount of permanganate solution necessary to oxidise the Ti_2O_3, formed by the reduction of this amount of TiO_2, the amount of permanganate employed to oxidise the niobium is found, and from this the amount of niobium can be calculated. The tantalum is found by difference.

In this way the following results were obtained :—

	Nb_2O_5.	Ta_2O_5.	TiO_2.
Taken	0·3357	0·2246	0·0687 gram
Found	0·3314	0·2289	0·0667 „

B. H. B.

Estimation of "Light Hydrocarbons and Non-nitrifiable Substances" in Commercial Benzene. By B. Nickels (*Chem. News*, **52**, 170—171).—For the purpose indicated in the title, the author recommends the use of the processes previously proposed (this Journal, 1881, 770, 950), with the addition of taking the boiling points of the benzene both before and after treatment, coupled with some unpublished methods. D. A. L.

Testing Essential Oils. By P. Carles (*J. Pharm.* [5], **12**, 529—530).—There are three principal methods in use for this purpose. 1. The essence is agitated with its own volume of a fatty oil, olive oil, &c. If the mixture remains clear, the essence is supposed to be pure, but if the mixture becomes turbid adulteration with alcohol is inferred. 2. The essence is agitated with its own volume of distilled water in a tube. The volumes of the two liquids are noted on the tube before shaking, and again after the tube has been allowed to remain for a few minutes. If alcohol is present, the volume of essence is diminished, and that of the water is increased. The author finds this method to be quantitative as well as qualitative. 3. A given volume of essence is agitated with a fragment of dried calcium chloride. The salt remains unchanged in pure essence, but in the presence of alcohol it becomes more or less liquid, according to the amount of this solvent present. The author finds that the first method may fail to detect as much as 20 per cent. of alcohol, whereas the second and third methods readily detect small quantities.

J. T.

Examination of Mustard Oil. By H. Hager (*Chem. Centr.*, 1885, 974).—The artificial mustard oil of commerce may be distinguished

from the natural volatile oil by its reactions in alcoholic solution with solution of mercuric nitrate. The natural oil gives a white or light-grey turbidity or precipitate, the artificial oil a dark-grey precipitate. W. R. D.

Determination of Glycerol. By W. Fox and J. A. Wanklyn (*Chem. News*, **53**, 15).—The aqueous solution of glycerol, containing not more than 0·25 gram of this substance, is made alkaline with 5 grams of solid potash, powdered potassium permanganate is then gradually added until the solution is permanently pink, and the whole is heated at the boiling point for half an hour. Under these circumstances 1 mol. of oxalic acid is formed for every molecule of glycerol present; the solution is treated with sulphurous anhydride, filtered, acidified with acetic acid, boiled, and precipitated with a calcium salt. The oxalic acid is determined in the precipitate by titration with standard permanganate in the usual way, and the amount of glycerol calculated from the result. D. A. L.

New Method of Detecting Oxalic Acid in Urine. By E. Salkowski (*Zeit. physiol. Chem.*, **10**, 120—122).—The precipitate obtained by Neubauer's method is found to contain besides calcium oxalate, calcium sulphate, chlorides, and urates. It may be separated from these impurities by washing with 80 per cent. alcohol, then with a small quantity of hot water, and dissolving in dilute hydrochloric acid. This solution is neutralised by ammonia and re-acidified with acetic acid. After 24 hours, a white precipitate settles, and this is found by microscopic examination to consist exclusively of well-formed crystals of calcium oxalate. W. D. H.

Simple Method for Detecting Adulterated Butter. By A. Mayer (*Bied. Centr.*, 1885, 851—854).—As the polarisation microscope is not a perfectly trustworthy test for adulterated butter, for under certain conditions pure butter has influence on the polarised ray, the author has devised the following method:—About 6 grams of butter placed in a test-tube is mixed with 12 c.c. of water, to which has been added 2 drops of 2 per cent. sodium hydroxide solution. After thoroughly shaking, the whole is heated on a water-bath at 37°; after another shaking, the emulsion is poured into a funnel, whose spout is closed by india-rubber tubing and a pinch-cock; then it is washed several times with water at 37°. When the water runs away clear, the butter is allowed to cool, when it ought to be in a finely-divided caseous condition; but if there is any adulteration, globules of fat will be observable and are also noticeable during the washing. In summer, the temperature must be slightly lower, for "grass butter" melts at a slightly lower temperature than the "winter butter." Another test may be used when colouring matter has been added, namely, treatment with alcohol, which dissolves the artificial colouring frequently added in winter. E. W. P.

Detection of Hydrocarbons in Fat and Oil. By F. Nitsche (*Chem. Centr.*, 1885, 976).—Ten grams of the oil or fat is saponified

with a mixture of 7 grams of aqueous soda (38° B.) and 30 grams of alcohol; 40 grams of glycerol is added by degrees to prevent the solidification of the soap. The liquid when cold is twice extracted with 10 c.c. of benzene, which, when evaporated, leaves the hydrocarbons. The process can be used quantitatively. W. R. D.

Titration of Urea by Means of Hypobromite after Hamburger's Method. By E. Pflüger and F. Schenck (*Pflüger's Archiv.*, **37**, 399—422).—Hamburger (Abstr., 1885, 450) described a process for the estimation of urea, which he asserted surpassed Pflüger's modification of Liebig's method. It consisted in adding an excess of a standard hypobromite solution to the solution containing urea, deoxidising the excess of hypobromite with sodium arsenite, and finally determining the amount of unoxidised arsenite by a standard solution of iodine.

In the present paper, the authors submit Hamburger's method and results to severe criticism; two very serious objections are raised: firstly, Hamburger failed to determine the amount of gaseous nitrogen evolved, and assumed, although not necessarily the case, that the oxidation in urine was proportional to the amount of nitrogen present; secondly, the standard hypobromite solution changes very rapidly, losing as much as 0·85 per cent. of its strength in a day.

A very large number of determinations were made with every precaution suggested by Hamburger, but in every case the results were most untrustworthy; the difference, which is always plus, varying from 2·7 to over 10 per cent. of the nitrogen present. The longer the interval between the addition of hypobromite and arsenite the greater the error. Hamburger did not sufficiently regard the error induced through the oxidation of other substances present in urine.

J. P. L.

Estimation of Urea. By G. Lunge (*Pflüger's Archiv*, **37**, 45—50).—A new form of "ureometer" is here described, which will be more convenient in medical practice than the other numerous instruments at present in use.

The use of the patent "bromum solidificatum" is recommended in the preparation of the solution of hypobromite of soda.

W. D. H.

Note.—No reference is made to a very similar instrument invented by A. W. Gerrard (Abstr., 1885, 610).—W. D. H.

Hüfner's Method of Estimating Urea. By E. Salkowski (*Zeit. physiol. Chem.*, **10**, 110—113).—In Hüfner's method, the urea is decomposed by means of a strongly alkaline solution of sodium hypobromite. In order to get all the nitrogen off, he waits half-an-hour. The operation can, however, be much shortened as follows:—The urine is diluted five or ten times, a quantity corresponding to 2·5 c.c. of urine is taken, and two drops of hydrochloric acid added; this is boiled until the flask is emptied of air; the proper quantity of hypobromite solution is added, and the mixture again boiled. The nitrogen comes off and is collected, and the operation completed in a

few minutes. The strongly alkaline solution contains only a minimal quantity of air, so that the error from this source is very small.

W. D. H.

Neubauer's Method of Estimating Creatinine in Urine. By E. Salkowski (*Zeit. physiol. Chem.*, **10**, 113—120).—Neubauer's method should be modified as follows:—240 c.c. of urine is rendered alkaline by the careful addition of milk of lime, and then precipitated with calcium chloride; the volume is made up to 300 c.c., and after 15 minutes filtered; of the filtrate, which must be feebly alkaline, 250 c.c. (= 200 c.c. urine) is evaporated to about 20 c.c., and an equal volume of absolute alcohol added. Subsequently, this is diluted to 100 c.c., allowed to remain 24 hours, and filtered. To 80 c.c. of the filtrate, solution of chloride of zinc is added, and so on as Neubauer describes.

The zinc creatinine chloride must be examined microscopically, to make certain of its being free from octahedra of sodium chloride, and should form a clear solution in hot water. Still further certainty may be obtained by estimating the zinc.

Creatinine appears to be a constant constituent of human urine, which indeed in some cases showed high percentages.

W. D. H.

Tests for Atropine. By Flückiger (*Pharm. J. Trans.* [3], **16**, 601—602).—Atropine, homatropine, and hyoscyamine show an alkaline reaction with phenolphthaleïn; the first two also precipitate solutions of mercuric chloride, but hyoscyamine does not. Cocaïne precipitates mercuric chloride, and is alkaline to litmus but not to phenolphthaleïn. Three tests for atropine are described:—(1) With sodium nitrate, sulphuric acid, and subsequently sodium hydroxide, producing a violet colour; (2) the same as 1, but with sodium nitrite instead of nitrate, producing an orange colour, which, on dilution with aqueous sodium hydroxide, changes to red, violet, or lilac; (3) with glacial acetic acid and sulphuric acid, when heated for a sufficiently long time, a greenish-yellow fluorescence is developed. D. A. L.

Assay of Quinine Sulphate. By J. E. De Vrij (*Chem. Centr.*, 1885, 968; comp. Abstr., 1885, 302).—The quantity of cinchonidine sulphate in commercial quinine sulphate may be determined in the following way:—5 grams of the quinine sulphate is dissolved in 11 c.c. of normal sulphuric acid at 60°. The solution is evaporated to the point of crystallisation and cooled. Enough distilled water is then added to replace the weight lost during evaporation. The cinchonidine is dissolved as acid sulphate, and may be separated from the clear liquid by precipitating with soda solution, and agitating with 25 grams of ether. The crystals of cinchonidine are dried and weighed. This method will detect 2 per cent. of cinchonidine in quinine sulphate. W. R. D.

Use of Metallic Oxides for the Detection of Coal-tar Colours in Wines. By P. Cazeneuve (*Compt. rend.*, **102**, 52—54).—The

oxides employed were yellow mercuric oxide in the proportion of 0·2 gram per 10 c.c. of wine; lead hydroxide, containing 50 per cent. of water, in the proportion of 2 grams per 10 c.c.; and gelatinous ferric hydroxide, containing 90 per cent. of water, in the proportion of 10 grams per 10 c.c. The foreign colouring matters were mixed with the wine in quantities not exceeding one-fourth of the total colouring matter. Some of the experiments were made at the ordinary temperature; in others the liquid was heated to boiling.

Mercuric oxide completely absorbs the natural colouring matter, cochineal, and foreign vegetable colours; erythrosin, eosin J, methylene-blue, Coupier's blue, and diphenylamine-blue. It partially absorbs orange I, safranine, chrysoidine, chrysoine, methyleosine, yellow II, red NN, red I, and ponceau RR. It does not absorb the sulpho-conjugated derivative of rosaniline, Bordeaux red B, soluble red, purple red, Biebrich scarlet, croceine 3B, ponceau R, ponceau B, orange R, orange RRR, orange II, orange RR, tropeoline M, tropeoline II, yellow I, solid yellow, dinitronaphthol-yellow, US yellow.

Lead hydroxide completely absorbs the natural colouring matter, cochineal, and foreign vegetable colours, methylene-blue, Coupier's blue, diphenylamine-blue, and erythrosin. It differs from mercuric oxide in not absorbing the rosanilines, and also in absorbing the sulpho-conjugated derivative of rosaniline, Bordeaux red B, the purple-red, and soluble red of rocelline.

Ferric hydroxide does not absorb erythrosin, the sulpho-conjugated derivative of rosaniline, Bordeaux red B, purple-red, soluble red, and solid yellow. It absorbs the natural colouring matter and foreign vegetable colours, cochineal, and all the derivatives of rosaniline, except the sulpho-conjugated derivative.

Zinc hydroxide and stannous hydroxide behave similarly. The latter retains the natural colouring matter, but does not absorb cochineal or orchil. After the wine has been treated with the hydroxides, the colouring matters must be distinguished by special tests. If the wine is treated with magnesia and hot amyl alcohol, a number of blues which are precipitated by the above-mentioned hydroxides can be isolated and distinguished. C. H. B.

Carmine. By M. Dechan (*Pharm. J. Trans.* [3], **16**, 511—512).—Carmine, the compound of alumina or tin with the colouring matter of cochineal, is met with in commerce adulterated with aniline-scarlet, vermilion, chrome-red, albuminous and starchy matters, and uncombined alumina, all of which, with the exception of the first, are insoluble in dilute ammonia. Hence the following method is recommended for the examination of carmine. The sample is exhausted with dilute ammonia which removes the carmine, the insoluble portion is dried and weighed, then treated with hydrochloric acid; the loss is uncombined alumina, lime, &c.; the ash and organic matter are determined in the residual matter. Ash and moisture are likewise determined in the original sample, and if necessary, the mercury. Aniline-scarlet dyes wool of a red-orange tint, whereas cochineal-carmine gives a purple-red; this admixture can be readily detected by boiling a piece of white woollen stuff for a half an hour in the

ammoniacal solution and examining the tint produced. The numerical relation of the combined alumina and lime to the colouring matter in carmine is not definite, as the combination is not purely chemical but of a physico-chemical nature. D. A. L.

Technical Chemistry.

Self-purification of Polluted Waters. By A. Müller (*Landw. Versuchs-Stat.*, 1885, 285—300).—As the self-purification of water is largely due to nitrification, the author undertook a research to determine the influence which organic matter has on the decomposition of urine through the action of the nitrifying ferment. For this purpose, cane-sugar, milk-sugar, starch, alcohol and acetic acid, were added to diluted urine, which was in active nitrifying decomposition. It was found that pure saccharose in pure water resisted strongly any molecular decomposition; this resistance was less strongly exhibited by lactose, and less still by rice-starch. Wood-ashes aids this decomposition, but less powerfully when the substance attacked is lactose, whilst it shields starch from change. When ammonium carbonate and wood-ashes were added to the mixture, the action on the organic matter was energetic, more so than when ammonium carbonate only was added. All the ammonia was nitrified in the solution containing acetic acid, two-thirds in the saccharose and starch solutions, and in the lactose solution the half of the ammonia was converted. Lastly, in spite of the reduction of the organic matter in acetic acid and lactose solutions in the presence of wood-ashes, the whole of the nitrogen was retained, whereas in the other solutions a loss of nitrogen occurred, whether the wood-ashes were present or not. It appears then that these carbohydrates and their derivatives check the nitrification of normal urine, and the destruction of the carbohydrates is assisted by alkalis and ammonia. E. W. P.

Various Bleaching Liquids. By G. Lunge and L. Landolt (*Chem. Ind.*, 1885, 337—346).—*Chlorozon.*—This substance, manufactured by passing chlorine mixed with air into caustic soda, and for which a high value as a bleaching agent has been claimed, is actually a solution of hypochlorous acid in sodium chloride, with traces of free chlorine and of sodium chlorate. Chlorous acid and chlorine peroxide are absent. Comparative experiments showed that the omission of the air-stream has no effect on its composition.

Products of the Action of Chlorine on Magnesia.—Dry or nearly dry magnesium hydroxide does not yield a bleaching powder when treated with chlorine. When chlorine is passed into a milk of magnesia at 15° or even at 0°, more than half of the absorbed gas goes to form chlorate (with the corresponding chloride), the remainder producing hypochlorite. At higher temperatures, or on warming the above

solutions, or even passing air through them, almost all the hypochlorite is converted into chlorate, a small portion decomposing into chloride and free oxygen. Neither chlorate nor free oxygen (except traces) is formed when chloride of lime is mixed with sulphate of magnesia.

Action of Chlorine on Zinc Hydroxide.—With the solid hydroxide only a trace of a bleaching compound is formed. With the hydroxide suspended in water, both hypochlorite and chlorate are formed, the latter in smaller proportion than in the case of magnesia. Heating converts the hypochlorite partly into chlorate, but the tendency to decompose into chloride and free oxygen is greater than with magnesia hypochlorite.

The solution obtained by mixing a zinc salt with chloride of lime is less stable than the corresponding magnesian solution.

Aluminous Bleaching Liquids.—Aluminium hydroxide does not absorb chlorine. The solution obtained by double decomposition contains chiefly hypochlorite, but part of this immediately spilts up into aluminium hydroxide and free hypochlorous acid.

Alteration on keeping.—Chloride of lime, and the solutions containing magnesium, zinc, and aluminium obtained from it by double decomposition, change very slowly in the dark, but on exposure to diffused daylight in closed vessels rapidly lose nearly the whole of their bleaching power.

Conversion of Chloride of Lime into Chlorate.—Simple boiling is insufficient; the formation of chlorate progresses very slowly, and more than half of the hypochlorite decomposes into chloride and oxygen. If, however, the liquid is saturated with free chlorine, 70 per cent. is at once converted into chlorate (with the corresponding chloride) in the cold, and although without heat the further progress of the change is very slow, yet on heating to boiling it is completed without loss of oxygen. Passage of chlorine during the heating is prejudicial.

Comparative bleaching experiments with the bleaching compounds of the above four metals showed that the zinc solution acts the most rapidly. The passage of carbonic anhydride for a short time, or the addition of a minute quantity of acetic or oxalic acid, accelerates the action immensely. When used in excess, the three acids seem to be about equally active. M. J. S.

Progress of the Action in Sulphuric Acid Chambers. By P. Naef (*Chem. Ind.*, 1885, 285—290).—At the works of Messrs. Sullivan and Co., Widnes, the author has repeated and confirmed the observation made by Lunge and himself (Abstr., 1884, 698), that by far the larger part (77—83 per cent.) of the sulphurous anhydride entering the lead chamber has disappeared by the time the gases have traversed half its length, whilst from that point to the end of the chamber a very trifling diminution takes place. The quantity of sulphuric acid deposited on a given area is, however, not proportional to the amount of sulphurous anhydride which has disappeared from the gases at that locality. Near the end of the chamber it is as much as at the middle, and only about twice as much at the entrance. That the amount of

acid collected at a given spot is not a measure of the reaction taking place there is shown by the following facts. When the collecting trays are protected from the perpendicular fall of drops of acid by shields at a distance of 4—12 inches, the same quantity of acid was collected as in uncovered trays similarly situated. This cannot be due to an oblique fall, since the motion of the gases is so slow that a sensitive Fletcher's anemometer failed to detect it. Moreover, as Mactear and others have also observed, the same amount of acid is collected on trays placed near the roof as on those near the floor. The explanation appears to be that the acid does not fall as rain at all, but exists in the form of mist, requiring time and contact with surfaces for its precipitation, and that its presence in this state hinders the oxidation of the sulphur dioxide. If this hypothesis is correct, it gives countenance to the patented process of Thiess, who passes his gases through mixing towers, and thence through numerous small perpendicular tubes, divided by horizontal perforated partitions, and claims to produce a large amount of acid in an apparatus of very small size. M. J. S.

Process for Hardening Castings in Gypsum. By M. Dennstedt (*Ber.*, 3314—3316).—The object is warmed at 60—80°, and then dipped into a hot saturated solution of baryta. The solution soaks into the gypsum, and on cooling deposits crystals of baryta, which change eventually into carbonate or other insoluble compounds. If greater hardness is required, free silicic acid or salts of metals which react with baryta with formation of insoluble metallic oxides or hydroxides may be used. N. H. M.

The Electrical Furnace and the Reduction of Oxides. By E. H. Cowles, A. H. Cowles, and C. F. Mabery (*Amer. J. Sci.*, **30**, 308—312).—The application of electricity to metallurgy has hitherto been confined to the reduction of metals from solution, and few attempts have been made to effect dry reductions by means of an electric current. The authors have now succeeded in obtaining a continuous high temperature by introducing coarsely pulverised carbon into the path of the current from a dynamo, in order to maintain a variable resistance. When the carbon, mixed with the oxide to be reduced, was made a part of the circuit in a fire-clay retort, and submitted to the action of a powerful current, the reduction was accomplished, and the temperature increased to such an extent that the interior of the retort fused completely. Experiments already made show that aluminium, silicon, boron, manganese, magnesium, sodium, and potassium, can be reduced from their oxides with ease. B. H. B.

Preparation of Aluminium. By M. Herzog (*Chem. Centr.*, 1885, 907—909).—Processes are described, which involve the use of metallic sodium for producing aluminium from the chloride and fluoride. The metal may also be obtained from the sulphide, which can be prepared by passing the vapour of carbon bisulphide over red-hot alumina. The sulphide is reduced to metal either by heating it

with iron filings or with anhydrous aluminium sulphate, when sulphurous anhydride is evolved and the metal liberated.

W. R. D.

Commercial Treatment of Roman Alunite. By P. Guyot (*Chem. News*, **53**, 27—28).—The constituents of alunite of use in the manufacture of alum, are alum, aluminium sulphate (basic), and free alumina. The ore is calcined, then treated with sulphuric acid and potassium sulphate, the alum being allowed to crystallise out, and the mother-liquors used over again. The heat of calcination must be modified according to the composition of the ore, inasmuch as the alumina is converted into the soluble form at a lower temperature than is required by the basic salts before they assume the soluble modification. Thus an ore of the following percentage composition, potassium sulphate 14·00, potassium aluminium sulphate 26·55, aluminium sulphate 6·56, alumina 18·58, water 11·90, ferric oxide 0·80, siliceous residue 21·61, gave better results on calcination at between 800—900° than at lower temperatures. The quantity of sulphuric acid required is gauged by the amount of potassium sulphate in the ore: for example, an ore containing 12·5 per cent. K_2SO_4 should not have more than 9·8 tons of sulphuric acid (52° B.) to eight tons of calcined mineral, a quantity somewhat in excess of the theoretical. The calcined ore is added in instalments to the excess of acid reduced to 30° B. and heated at 80—90°, digested for two hours, concentrated to 38° B., potassium sulphate added, and after 13 hours the supernatant liquid is drawn off; this should not be more than 41° or 42° B. The alum is separated, &c. When the mother-liquors become very impure, it is best to recover the acid by the preparation of secondary products.

D. A. L.

Connection between Illuminating Power, Flashing Point, and Boiling Point of Petroleum. By C. Engler (*Chem. Ind.*, 1885, 44—49).—In 1883, simultaneously with the raising of the minimum legal flashing point of petroleum from 15° to 21° (Abel's test) in Germany, a considerable deterioration in the illuminating power of American oils took place. Fractional distillation of numerous samples showed that a higher flashing point had been gained not simply by the rejection of the more volatile oils, but by the inclusion of a larger proportion of heavy oils. From 23 specimens examined between 1879 and 1882, an average of 22·95 per cent. (vol.) distilled below 150° and 11·5 per cent. above 300°; whilst 25 samples purchased in 1883-4 gave 15·1 per cent. below 150° and 25·4 per cent. above 300°. It is these heavy oils which are so prejudicial. They cause not only an immediate loss of illuminating power, but a very serious falling off when a lamp is allowed to burn for several consecutive hours. This falling off is partly due to the deposition of carbon on the wick, which occurs only with oils boiling above 300°, and partly to an increase in the viscosity of the oil as the consumption proceeds. On the other hand, their effect in raising the flashing point is small compared with that which would result from the removal of the more volatile oils.

A Russian oil from Baku, of flashing point 34°, yielded only 7 per cent. below 150° and 4·5 per cent. above 300°, and the author considers that such oils will enter into very serious competition with the American, unless the latter speedily show an improvement.

M. J. S.

Obtaining the Sugar from Molasses. By STERNBERG and C. HEYER (*Bied. Centr.*, **15**, 65—66).—A process for the recovery of sugar has been highly praised; it depends on the use of an acid and a large quantity of strong alcohol, and professes to obtain 30 per cent. of the 50 per cent. of sugar contained in the molasses in the space of 7—8 hours, with a loss of only 3 per cent. of alcohol; the details of the process are concealed with the greatest secrecy.

Sternberg has been trying to investigate the process, and thinks that it is a modification of the older one of Marguerite, discovered 17—18 years since, in which 100 kilos. of molasses was mixed with 100 litres of 85 per cent. alcohol and 5 kilos. sulphuric acid, the salts, potash especially, were precipitated, the sugar remaining in solution. After filtration more alcohol (100 litres) was added, and the sugar was either left to slowly crystallise, or some more sugar from a former process added which greatly hastened the operation.

Heyer reports unfavourably of the new modification of the strontium process as carried out by Lebaudy, in which, instead of adding to the molasses crystallised strontium hydroxide, caustic soda is first employed and a strontium salt then added. He considers the amount of sugar recovered to be less than by the old process, the chemicals dearer, and the change decidedly less advantageous from a financial point of view.

J. F.

Dyes obtainable from the Tannins and their Derivatives. By O. N. WITT (*Chem. Ind.*, 1885, 100—105).—A sketch is given of the sources and mutual relations of tannin, gallic, pyrogallic, and ellagic acids, and their earlier known coloured derivatives, rufigallol, anthragallol, and gallocyanin. In dyeing with gallocyanin, the use of the costly chromium acetate as a mordant has been replaced by sodium chromite, from which cotton-fibre possesses the power of appropriating the chromium oxide. The goods are padded with an alkaline solution of the chromite mixed with glycerol, and after being left in rolls for a short time, are steamed. After washing they are ready for the gallocyanin bath, which produces a deep violet; the addition of some extract of Persian berries gives an indigo shade.

Passing to gallein and cœrulein, it is mentioned that the soluble cœrulein of commerce is a compound with an alkaline hydrogen sulphite, but that it is preferable to use the commercial paste, and form the soluble compound in the printing colour.

Other dyes have been obtained from pyrogallol, but have as yet received no practical application; thus, benzaldehyde furnishes a blue, acetaldehyde a redder dye, whilst furfural and hydrochloric acid give an indigo-blue mass, dissolving in water with fine green colour. Reichl has obtained a dye by heating pyrogallol with glycerol and sulphuric acid. With nitrosodimethylaniline, it yields a violet which

is inferior to gallocyanin; diazobenzene nitrate affords an orange-yellow; a blue is also produced by the action of alkalis on amido-pyrogallol.

All the above-mentioned compounds are produced from the iron-bluing tannins, but the less studied iron-greening tannins also yield dyes. Thus, the catechins furnish intense brown dyes when oxidised by potassium dichromate; by warming with nitrosodimethylaniline, they produce violets resembling gallocyanin, and by the action of diazobenzene a brown-red azo-colour.

Maclurin and the tannin of horse-chestnuts similarly treated also afford coloured products. M. J. S.

Dust Explosions. By C. Engler (*Chem. Ind.*, 171—173).—Solid bodies, such as soot, lampblack, and wood charcoal, which evolve no combustible gas when heated, are incapable of producing an explosion or even of extending a flame, when they are dispersed through air as a cloud of fine dust. Heating the air previously to 300° makes no difference. The addition, however, of a combustible gas, in proportion too small to form by itself an explosive mixture with the air, causes the flame to extend through the entire mass with explosive rapidity. On the other hand, powders capable of yielding a combustible gas, such as coal and flour, can by themselves form explosive clouds. M. J. S.

General and Physical Chemistry.

Effect of Various Dyes on the Behaviour of Silver Bromide towards the Solar Spectrum. Connection between Absorption and Photographic Sensitiveness. By J. M. Eder (*Monatsh. Chem.*, **6**, 927—953).—The following conclusions are drawn from the results of a large number of experiments described in the paper:—

The absorption-spectrum of the dye in alcoholic or aqueous solution, or in the dry gelatin plate, does not coincide with the position of the maximum of sensitiveness on dyed silver bromide gelatin, which was always found to be more towards the red than the maximum of absorption of the solutions examined. The reason of this shifting is probably due to the much greater density of the silver bromide (= 6·353) than that of the gelatin (= 1·326).

Those rays which effect the maximum decomposition of dyed silver bromide have, on an average, wave-lengths 30-millionths of a millimetre shorter than those which are absorbed by the dyed gelatin (without silver bromide).

Those rays which are absorbed by silver bromide containing eosin have the same wave-lengths as those for which the dyed silver bromide shows increased photographic sensitiveness.

Dyes may be classified in the following way:—

1. Dyes which absorb the spectrum from the violet gradually onwards, and whose sensitising action follows closely, without maximum, the ordinary photographic action: soluble Prussian blue, Poirier blue, aniline-blue, chrysaniline, various ponceaus, curcuma, neutral violet, chrysoline, diazo-amidobenzene, jasmine, acid orange, &c.

2. Dyes which show an absorption band in the spectrum and a corresponding sensitising maximum shifted toward red: eosin colours, cyanosin, methylerythrin, phloxine, rose Bengal, aniline-red, naphthalene-red, cyanine, resorcinol-blue, coralline, Coupier blue, safranine, methyl-violet, acid-violet, methyl-green, acid-green, many ponceaus, &c.

Silver bromide in a gelatin plate dyed with naphthol-blue, has the greatest sensitiveness of all known photographic preparations for light of different wave-lengths; the sensitiveness extends without interruption from λ3600—7600. This way of sensitising silver bromide is best adapted for photographing the less refractive rays, but also answers very well for the blue end of the spectrum.

The results above given confirm Vogel's absorption theory, and give the following law for the sensitising action of dyes on silver bromide. Many dyes sensitise silver bromide (or chloride), the increased sensitiveness towards coloured light being determined by the absorbing power of the dye towards the light; those rays which are absorbed by dyed silver bromide have the same wave-lengths as those for which the dyed silver bromide shows increased photographic sensitiveness. A narrow or broad absorption band gives a

similar one in sensitising. The sensitiveness of silver bromide gelatin for rays of longer wave-length can be increased by some dyes, as, for instance, naphthol-blue, to such a degree that it extends uninterruptedly over the whole spectrum, from the extreme red to the ultra-violet. N. H. M.

Dispersion Equivalent of Sulphur. By A. Schrauf (*Ann. Phys. Chem.* [2], **27**, 300—314).—In this paper, the various formulæ proposed for the determination of the dispersion equivalents are discussed with especial reference to the sulphur-derivatives of the paraffinoïd hydrocarbons. The nearest approximation of the observed and calculated values is obtained by the formula $MB\delta^{-2}$, in which M is the molecular weight, and B the second constant of Cauchy's dispersion formula. Secondly, in homologous series of compounds containing carbon, hydrogen, and oxygen, the value of the dispersion equivalent is best deduced by a process of summation. The formula $MB\delta^{-1}$ gives the worst results; $MB\delta^{-3}$, almost absolutely concordant results; whilst those obtained by the formula $MB\delta^{-2}$ are within the limits of experimental error. Thirdly, in homologous series of carbon, hydrogen, and sulphur compounds, the values for the dispersion equivalent calculated from the formula $MB\delta^{-2}$, and the refraction equivalent from the well-known formula of Lorenz $\frac{Mn^2-1}{(n^2+2)}\delta$, are identical with those of prismatic sulphur. The author considers that differences of constitution of carbon compounds are evidenced more markedly by their dispersion than by their refraction equivalents.

V. H. V.

Variation of Specific Rotatory Power. By A. C. Oudemans, Jun. (*Rec. Trav. Chim.*, **4**, 166—180).—In a former paper (Abstr., 1883, 81), the author has shown that the specific rotatory power $[\alpha]_D$ of the mono- and bi-acid bases, in the case of their normal salts, is independent of the nature of the acid with which the base is united, provided that the relative concentration in terms of the base is the same. In this paper, the converse case is considered of the different salts of the same acid; a similar generalisation is found to hold good for the salts of quinic and podocarpic acids examined by the author, and for camphoric and tartaric acids quoted from Landolt's researches. The principal exception is tartar emetic, a similar anomaly to which in the case of potassium antimonyl malate has been shown by Pasteur. As a further point, experiments are quoted to show that the specific rotatory power of tartaric acid is unaltered by the addition of a quantity of base more than sufficient for its complete neutralisation.

V. H. V.

Observations on Millot's Note on the Products of the Oxidation of Carbon in the Electrolysis of a Solution of Ammonia. By A. Bartoli and G. Papasogli (*Compt. rend.*, **102**, 363).—The authors point out that in their experiments (*Gazzetta*, **13**) sodium chloride was added to the solution of ammonia in order to increase the conductivity of the liquid. Millot's experiments (Abstr., 1885, 1125) were not made under the same conditions.

C. H. B.

Electrolysis of Salts. By A. Renard (*Compt. rend.*, **102**, 361—362).—The experiments were made with the apparatus previously described (*Compt. rend.*, **101**, 747). In dilute solutions, when other conditions are constant, the quantity of metal precipitated in unit time increases with the temperature in accordance with the formula $P_t = P_0(1 + K_t)$, in which K increases as the concentration diminishes. When the solutions are so dilute that the quantity of metal precipitated at a given temperature is proportional to the concentration, K attains a maximum value of 0·052.

In very dilute solutions, if the distance between the electrodes is successively doubled, the quantity of metal deposited decreases in geometrical progression, the common ratio of the series being 1·237. This law, however, does not hold good for distances greater than 320 mm., beyond which the values of the ratio increase somewhat rapidly.

The electrolysis of solutions of copper nitrate and sulphate with electrodes consisting of similar discs of copper, indicates that when the two electrodes are identical, the quantities of metal precipitated are proportional to the diameters of the electrodes, and therefore to the square roots of their surfaces. C. H. B.

Electrical Conductivity of Double Salts. By E. Klein (*Ann. Phys. Chem.* [2], **27**, 151—178).—Determinations by independent physical methods such as of change of volume and density (Kremers), of heat of dissolution (Favre and Valson), of lowering of freezing point (Raoult), and of dialysis (Ingenhoes), equally show that a double salt is either wholly or partially dissociated into its component salts when dissolved. As a further method for the solution of this problem, the author has determined the electric conductivity of solutions of certain metallic salts taken separately, or mixed together in molecular proportions, or lastly, in the form of a crystalline double salt. The main results of the examination by this method are as follows:—

(i) In the case of two salts, capable of a possible double decomposition, such as sodium or ammonium chloride with potassium nitrate, or potassium chloride with ammonium or sodium nitrate, the electric conductivity of the mixture, when in dilute solution, is approximately equal to the arithmetical mean of the conductivity of those salts presumably present in such a solution.

(ii) Conversely, from the determination of the conductivity of an unknown mixture, conclusions can be drawn as to the nature of the salts present.

(iii) The conductivity of the double salts examined, such as the double sulphates of the alkali metals and those of the magnesium group, is in the case of dilute solution slightly less than the arithmetical mean of the conductivity of these salts taken separately, the diminution increasing proportionally with the concentration of the solution. This result indicates that such double salts are dissociated completely in dilute, but partially in concentrated solutions; the degree of dissociation increases with the temperature. V. H. V.

Electrolysis of some Chemical Compounds. By D. Tommasi (*Bull. Soc. Chim.*, **45**, 144—146).—If an aqueous solution of potassium chlorate, acidified with sulphuric acid so dilute that when treated with metallic zinc no reduction of the chlorate takes place, is submitted to electrolysis, the anode being formed of pure zinc, reduction occurs and potassium chloride is formed, although if the electrolysis is conducted with platinum electrodes no such action takes place. The reduction is therefore due to the direct union of the zinc with the oxygen of the chlorate, and not to the action of nascent hydrogen. Potassium perchlorate is not reduced by electrolysis even when a zinc electrode is employed. A dilute aqueous solution of chloral hydrate in a porous cell placed in a vessel of water acidified with sulphuric acid was electrolysed, the cathode being placed in the chloral and the anode in the water; chlorine and free hydrogen were given off at the cathode, and aldehyde was formed. A. P.

Expansion Coefficient of Sulphur. By A. Schrauf (*Ann. Phys. Chem.* [2], **27**, 315—320).—The expansion coefficients of the crystallographic axes of prismatic sulphur are commensurable with the axes themselves, namely, there exists an identical proportionality between the coefficients and the axes, if the crystallographic form be represented by the symbol $[\delta P = 881]$.

As regards the relation between the expansion coefficients of allied elements, the determinations obtained by Fizeau for sulphur, selenium, and tellurium, are quoted to show that the coefficients increase with decrease of atomic weight. In the case of antimony and bismuth, it is shown that the proportionality between the crystallographic axes and expansion coefficients is either that of equality or of a simple integral ratio. V. H. V.

Law of Thermal Constants. By D. Tommasi (*Bull. Soc. Chim.*, **45**, 141—144).—The heats of formation of the picrates recently determined by Tscheltzow (Abstr., 1885, 1103) are practically identical with those which might have been predicted from the law stated by the author (Abstr., 1882, 1257), who further predicts the heats of formation of a large number of other picrates, phthalates, isophthalates, terephthalates, and chlorates. A. P.

Thermochemistry of Hypophosphoric Acid. By A. Joly (*Compt. rend.*, **102**, 259—262). — *Hydrated hypophosphoric acid*, $P_2O_4,4H_2O$, heat of solution at 10—11°, −2·2 cal.; heat of solidification at 11°, + 8·8 cal.

Normal hypophosphoric acid, $P_2O_4,2H_2O$, heat of solution at 11°, + 7·7 cal., from which it follows that $P_2O_4,2H_2O + 2H_2O$ sol. = $P_2O_4,4H_2O$ sol. develops + 7·0 cal.

The action of dilute solutions of sodium hydroxide on solutions of the acid and its mono-sodium salt, gives the following results:—

$PO_2{\cdot}H_2O$	+ $\frac{1}{4}Na_2O$	develops	+ 7·57 cal.
,,	+ $\frac{1}{2}Na_2O$	,,	+ 15·05 ,,
,,	+ $\frac{3}{4}Na_2O$	,,	+ 21·36 ,,
,,	+ Na_2O	,,	+ 27·11 ,,
,,	+ $1\frac{1}{2}Na_2O$	,,	+ 27·65 ,,

The heat developed by the first, second, and third equivalents of alkali respectively is 15·05, 12·06, and 0·54 cal. From these results, it follows that hypophosphoric acid is bibasic. Its heat of neutralisation closely approaches those of the other acids of phosphorus, and the difference between the thermal disturbances produced by the first and second equivalents of alkali is analogous to the differences observed by Graham, Berthelot, and Thomsen in the case of the other acids of phosphorus and arsenic. The development of heat caused by the addition of the third equivalent of alkali is due to the instability of the di-sodium salt. C. H. B.

Heat of Combustion of Amines. By A. Muller (*Bull. Soc. Chim.*, **44**, 608—611).—The heats of combustion and formation of the following amines were determined, Berthelot's calorimeter being employed:—

	Heat of combustion of the molecule.		Heat of combustion of one gram.	Heat of formation of the molecule.
	Gas.	Liquid.	Gas.	Gas.
Monomethylamine	256·9	—	8·276	9·6
Dimethylamine	426·0	—	9·458	3·5
Trimethylamine.....	577·6	—	9·783	14·9
Diethylamine.....	724·4	716·9	9·918	31·1
Triethylamine	1047·1	1038·3	10·363	34·4
Monisoamyline	876·4	867·6	10·069	42·1

The heat of substitution of the alcohol radicles for the hydrogen of the ammonia is also calculated for each of these amines. A. P.

Heat of Combustion of Benzene. By F. Stohmann, P. Rodatz, and H. Herzberg (*J. pr. Chem.* [2], **30**, 241—260).—The heat of combustion of liquid benzene at 17° is shown by a number of experiments to be 779799 cal., and that of gaseous benzene (also at 17°), 787488 cal. When the latter is corrected for the heat of evaporation and the molecular heat of liquid benzene at the temperature employed, it gives 779262 cal. for the heat of combustion of liquid benzene; the two results are, therefore, practically identical and agree very nearly with those of Berthelot, who estimated the heat of combustion of liquid benzene at 776000 cal., and with those of Thomsen, who obtained the number 787950 cal. (Abstr., 1882, 722). The higher values which Thomsen obtained (compare Abstr., 1881, 135, and Thomsen, "Thermochem. Untersuchungen," **4**, 59), as well as that given, are perhaps due to heat carried over from the burner used in warming the benzene to the calorimeter. N. H. M.

Calculation of Corrections for Bunsen's Ice Calorimeter. By L. Boltzmann (*Annalen*, **242**, 125—128).—Details of formula for corrections in determinations by this instrument.

Do the Statical and Dynamical Methods of Measuring Vapour-pressure give Identical Results? A Reply to G. W. F. Kahlbaum. By W. Ramsay and S. Young (*Ber.*, **19**, 69—74).—Kahlbaum's contention is, that the curve which represents the relations between temperature and pressure, when a liquid is caused to boil under different pressures, is not identical with the curve representing the same relations when the vapour of the liquid is allowed to exert its own pressure, as in the usual method of measuring vapour-pressures in a barometer tube. In Kahlbaum's experiments, the liquid is made to boil under different pressures in a flask, the vapour alone coming in contact with the thermometer; whilst to prevent bumping, a current of air is caused to bubble through the liquid. The results so obtained agree fairly well at higher pressures with those of other observers; but at low pressures the temperatures observed by Kahlbaum are invariably higher than previous observations have shown; the discrepancy is greater the lower the pressure, and becomes extreme when the true boiling point falls below the temperature of the surrounding atmosphere. In their first paper (*Ber.*, **18**, 2855—2858), the authors pointed out the great discrepancy between the results obtained for alcohol by Kahlbaum, and by Regnault and themselves; to which Kahlbaum replied that a difference, on his theory, ought to be observable, and that it was not caused by the "mechanical" superheating of the vapour by the current of hot air surrounding the ebullition flask. He also asserts that the method employed by the authors (Trans., 1885, 42), in which facility is given for the evaporation of the liquid from a free surface, is not a truly dynamical one; but his reasons for this assertion appear to the authors to be unsatisfactory. In their reply, the authors adduce measurements of the vapour-pressures of liquid acetic acid, in which identical results were obtained by the statical and dynamical methods (*Phil. Trans.*, 1884, ii, 461). They then refer to Thomson's theory regarding the continuity of the gaseous and liquid isothermals, in which he supposes that it is theoretically possible for a vapour to be exposed to a pressure higher than its vapour-pressure without liquefying, and also for a liquid to exist at a pressure lower than its vapour-pressure without assuming the gaseous state; they suggest that Kahlbaum has partially realised the second condition of matters, well known in the usual phenomenon of boiling with bumping, and that the numbers he gives have no value, inasmuch as they refer to no particular portion of this curve. Where the temperature of the escaping vapour in Kahlbaum's experiments should fall below that of the atmosphere, there can be no doubt that the vapour is heated by the atmosphere, and by the heated walls of the distillation bulb. Attempts to maintain a constant low temperature, by the vapour of a volatile liquid boiling at a temperature lower than that of the atmosphere, have failed in Regnault's hands, as in their own.

The laws showing the relationship between the vapour-pressures of various liquids appeared in the Transactions (1886, p. 37). The proofs are given in *Phil. Mag.*, December, 1885, and January and February, 1886. W. R.

The Law of Density Numbers. By J. A. Groshans (*Rec. Trav. Chim.*, **4**, 1—31, 153—166, 307—331). — These papers are an extension of the author's former observations on the application of his law of density numbers for the determination of boiling and melting points, and certain phenomena of solution (compare this vol., p. 194).

(I.) *Boiling points.*—Further examples are given of the application of the formula $T = 273 + t = 27{\cdot}8M/n\sqrt{m}$ (or $\sqrt{m + x}$), in which n is the sum of the density numbers of atoms of the elements composing the liquid, m the molecular weight, and x or $x + m$ constants.

In a series of tables, the observed boiling points and those calculated from this formula for certain paraffinoïd alcohols and their ethers, the phenols and their ethers, and the acids of the acetic series, are compared. As an incidental point, it is noticed that a paraffinoïd alcohol and an ether of the same general formula, but containing three CH_2-groups more, have the same value for the constant Tn/M.

(II.) *Phenomena of Solution.*—Thomsen, in his "Thermochemische Untersuchungen," has pointed out that the relation between the quantity of a substance (in gram-molecules) in solution and that of the solvent (in the same units) is expressible by the formula $r = \frac{Mn + a}{d} - Mn$, in which M and a are the molecular weights of the solvent and the substance dissolved respectively, and d the density of the resultant solution. The difference between the first and second factors on the right hand side of the equation (r) constitutes what is termed by Thomsen the "*residue.*" By means of the experiments of Thomsen, Nicol, and others, the empirical values for r can be determined. It is obvious that three possible cases arise—namely: (i) $r = a$, (ii) $r < a$, (iii) $r > a$, or expressed in language, the density of the resultant solution is equal to, less or greater than, that of the solvent. In the first of these papers the relation between these so-called residues and the density numbers is discussed, and it is shown by a series of equations, for which the reader is referred to the original memoir, that this relation is expressible by an empirical formula, $r = a + 18M - 6B\gamma$ (for the particular case of water), in which γ is a constant of value about 1·13, M another constant, generally a small positive or negative integer, and B the sum of the density numbers of the constituent elements of the compound entering into solution. In the papers cited above, a series of tables are given illustrating the application of this formula, thus demonstrating the relation between the law of density numbers and the phenomena of solution.

Melting points.—In the last of the above papers, it is shown that the relation between the density numbers and the points of fusion in absolute temperature scale is expressible by an equation, $T' = 27{\cdot}8M/n\sqrt[\theta]{m}$, in which the value for the exponential constant θ is generally 4, whilst that for m varies for each series of analogous elements or homologous compounds. The degree of accordance between the values observed and those calculated from the above formula is exemplified in the case of the elements in the following

table, it being assumed that their atomic and molecular weights are identical:—

Element.	M.	B.	*m*.	T′ calculated.	T′ observed.
Mercury	200	26	1	− 38·9°	− 39°
Bromine	80	9	1	− 2·5	− 7
Phosphorus..	31	3	1	+ 41·4	+ 44
Iodine	127	14	4	117·4	113—118
Potassium ..	39	8	4	62·6	62·4
Aluminium ..	27	4	4	598·4	600·0
Lithium	7	2	4	178·8	180·0

In the original memoir, a series of tables are given illustrating the above formula from the data given by Krafft for the paraffinoïd hydrocarbons, ketones, and acids of the acetic series.

It is further pointed out that the application of the formula renders intelligible the very gradual increase of temperature of fusion with increase of molecular weights in the homologous series.

V. H. V.

New Method for Determining the Specific Gravity of Gases, and for their Analysis. By F. Lux (*Zeit. anal. Chem.*, **25**, 3—10).—The apparatus, which the author names a baraeometer, consists of an ordinary hydrometer, carrying at its summit a globe of considerable size. It floats in water contained in a glass cylinder, the upper part of which is filled with the gas. The greater the specific gravity of the gas the higher will the float rise. The stem is graduated by using gases of known density. With a globe of 300 c.c. and a stem whose sectional area is 4 square mm., the difference of level for hydrogen and air respectively will be about 93 mm. The cylinder is furnished with stopcocks for passing a constant stream of gas through it, and by connecting several such cylinders in series, with suitable absorption apparatus between them, the alterations in specific gravity consequent on the removal of individual constituents of a mixed gas can be observed and the original composition thence deduced.

M. J. S.

Specific Gravity of Aqueous and Alcoholic Solutions of Mercuric Chloride. By J. Schröder (*J. Russ. Chem. Soc.*, 1886, 18—25).—The subjoined tables give the sp. gr. of aqueous and alcoholic solutions of mercuric chloride compared with water at 4°:—

Aqueous Solutions.

Per cent.	0°.	10°.	20°.	30°.
1·22	1·01008	1·00990	1·00835	1·00575
2·434	1·02035	1·02018	1·01856	1·01585
3·578	1·03050	1·03022	1·02855	1·02577
4·725	1·04070	1·04033	1·03856	1·03566

Alcoholic Solutions.

Per cent.	0°.	10°.	20°.	30°.	Coefficient of the change of sp. gr.
0	0·83135	0·82286	0·81435	0·80594	0·000849
1·22	0·8397	0·8312	0·8228	0·8141	0·000854
2·38	0·8484	0·8399	0·8314	0·8227	0·000858
4·42	0·8635	0·8549	0·8403	0·8375	0·000867
8·56	0·8966	0·8877	0·8789	0·8698	0·000891
12·43	0·9308	0·9213	0·9119	0·9024	0·000946
15·91	0·9620	0·9523	0·9425	0·9329	0·000971
19·32	0·9951	0·9852	0·9753	0·9652	0·000997
22·46	1·0285	1·0184	1·0083	0·9982	0·001013

A. T.

Correlation of Physical Properties of Solution with Concentration. By D. Mendeléeff (*Ber.*, **19**, 370—389, and 400—406).—As an introduction, the correlation of the sp. gr. of sulphuric acid with its concentration is discussed; but the mathematical formulæ given by various writers are found to be very complex in many, and unsatisfactory in all cases. The question then naturally arises as to the cause of such an apparently simple phenomenon as the variation of sp. gr. with concentration not being reducible to an uniform generalisation. It appears to the author, that the explanation can be traced to a frequent interchange of the components of the molecules present in the solution, which are not, as hitherto assumed, merely formed by simple juxtaposition. These molecules then, must be considered to be not statical, but dynamical units, the mass of which, taken as a whole, is in equilibrium. This interchange of molecules constitutes a phenomenon analogous to the movement of gas particles according to the mechanical theory developed by Clausius and Maxwell. But as these coalitions of molecules, as regards their formation and reciprocal interchange, are conditioned by the law of multiple proportion, then, under certain circumstances of composition, M_m with N_n for example, the interchange between M and N attains a maximum or minimum, characterised in a curve representing specific gravity in terms of composition as maxima or minima point or points of inflection. These points would also be rendered evident by various physical properties of the solution, such as heat of dilution, coefficient of refraction, and cohesion or capillarity.

Such phenomena the author intends to make an especial subject of investigation, and in these papers he deals particularly with the physical properties of solutions of sulphuric acid.

1. *Correlation of Concentration with Density.*—The curves expressing the values $\frac{d\frac{p}{s-s_0}}{dp}$, in which p is the percentage proportion, and s and s_0

the specific gravities of the solution and of water respectively, or $\frac{ds}{dp}$ show three points of inflection corresponding with the compositions $H_2SO_4 + 100H_2O$, $H_2SO_4 + 2H_2O$, and H_2SO_4, the intermediate one of the three, or that of greatest contraction, has previously been noticed by Ure, Kopp, Kolbe, and others.

2. *Heat of Dilution.*—The experiments of Thomsen on the thermic effects of mixing sulphuric acid with water illustrates what has been said above as regards the minimum and maximum heat changes corresponding with the composition $H_2SO_4 + 100H_2O$ and $H_2SO_4 + 2H_2O$. By the aid of various data given in a table, the interdependence of the heat changes with dilution and contraction is illustrated. Thus the maximum contraction at or about the composition of the hydrate $H_2SO_4 + 2H_2O$ is also that of the maximum heat development for the reaction between sulphuric anhydride and water in terms of 100 vols. of the solution, as also for the reaction between sulphuric acid, H_2SO_4, and water. But even though this hydrate, $H_2SO_4 + 2H_2O$, may be separated in a crystalline form, yet this fact will not warrant the assumption that in all solutions of sulphuric acid this hydrate is present as such; but only that in the association of molecules of sulphuric acid with those of water, the ratio of $1H_2SO_4$ to $2H_2O$ is characterised by a change in physical properties.

V. H. V.

Dissociation of the Hydrate of Hydrogen Bromide. By H. W. B. Roozeboom (*Rec. Trav. Chim.*, **4**, 331—347).—This paper is a continuation of the author's former experiments on the dissociation of the hydrate of hydrogen bromide and its solution under various conditions of temperature and pressure (compare this vol., p. 117). The curve representing the tension of dissociation in terms of temperature has three points of inflection, the first of which corresponds exactly with the molecular ratio $HBr : 2H_2O$, and is characterised by the fact that below this point the fusion of the hydrate is accompanied by an evolution of gas, and consequently an increase of volume; whilst above it there is an absorption and corresponding diminution of volume. The second point corresponds with the liquefaction of the gas, a phenomenon which determines a sudden change in the composition of the solution and its volume. The third point, which does not apparently correspond with any particular change of concentration or density, is that from which the tension increases uniformly with the temperature.

V. H. V.

Relative Permeability of Various Diaphragms. By A. Zott (*Ann. Phys. Chem.* [2], **27**, 229—289).—This lengthy memoir contains an account of elaborate experiments on the relative permeability of various diaphragms, such as marble, sand, clay, cork, coal, asbestos, parchment paper, pig's bladder, and goldbeater's skin. The advantages of each of these materials under various conditions are fully discussed, and from the quantitative results attained on the dialysis of different crystalline and colloïd substances, the following conclusions are arrived at:—(i) The most useful, homogeneous and watertight material as a dialyser, is goldbeater's skin, which is

twice as effectual under the same conditions as parchment paper, hitherto considered on the authority of Graham to be the best substance. But in the case of solutions which attack organic membranes, ordinary clay cells are the most useful, although their permeability is 60 to 75 times less than that of goldbeater's skin. (ii) The rapidity of the diffusion is increased by the complete exhaustion of the air collected within the pores of the dialyser; the rapidity is also dependent rather on increase of volume of the solution than on increase of mass dissolved. After a preliminary exhaustion, endosmose takes place even in the case of slowly diffusible substances, such as the so-called colloids. (iii) Two or more substances present in a solution are more rapidly and completely separated the greater the difference of their diffusion velocity; the terms colloïd and crystalloïd are purely relative. (iv) Separation by dialysis is more rapid the more often the liquid in the outer vessel is renewed. (v) With decrease of concentration, the diffusion velocity of salts, whether dissolved separately or admixed, decreases up to a certain point, from which it again increases slowly. These results are illustrated by many series of comparative experiments, collected together in various tables. V. H. V.

Contact Actions. By D. Mendeléeff (*Ber.*, **19**, 456—463).—It is a generally received opinion that not only the molecules as a whole, but each of the constituent atoms are in motion, the movement of the latter being conditioned by the limits of the molecule. If the conception be reasonable, then in every state of aggregation there are presumably motions of two kinds, the one internal, the other superficial. The contact of two molecules, as also conditions of temperature, pressure, and electric potential, influence each kind of motion; thus the phenomenon of catalytic or contact action gradually passes into that of dissociation or of decomposition. Herein the decomposition of hydrogen peroxide is analogous to that of many detonating solids, in which a disturbance of atom-equilibrium at the superficies of the molecule causes its complete disruption.

Now supposing two substances, A and B, are in superficial contact with one another under such conditions that not only the superficial movement of the constituent parts, but also of the molecule as a whole, is disturbed; then three distinct cases are possible.

Firstly.—The atoms change their kind of motion without returning to their former state of equilibrium; no chemical change ensues, but merely a physical phenomenon, such as alteration of electric potential, condensation of gases, whether by a cold surface or by porous substances.

Secondly.—The internal movement of the molecules is altered, so that molecules of a different kind are formed by combination, replacement, or decomposition. These changes are accompanied by an alteration of the energy of the system, but although the total heat effect observed is the algebraical sum of the energy changes, conditioned by the several changes of motion, yet thus far it is not possible to assign to each particular change its peculiar heat effect. As an example of chemical changes induced by the mere superficial

contact of the molecule as a whole, the author quotes the well-known experiments of Spring on the combination of metals with sulphur by mere pressure.

Thirdly.—The motion of the atoms within the molecule taken by itself can be of such a kind as to produce a chemical change or formation of a molecule of a different kind, such as the so-called isomeric transformation. Or again, the superficial contact of B with A, a mixture of heterogeneous molecules may cause either a decomposition or a combination between them, as exemplified in the experiments of Hautefeuille and Lemoine, which demonstrate that the presence of porous substances can induce the combination of hydrogen with iodine, and conversely the decomposition of hydriodic acid, both reactions attaining a limit. Of a similar nature is the combination of hydrogen with oxygen, induced by contact with finely divided platinum, and also the recent experiments of Konovaloff (this vol., p. 9), on the decomposition of haloïd derivatives of pentane by contact with materials in a state of fine division. These phenomena are generally classified under the title of catalytic or contact actions. Such can only be explained on the hypothesis that a stable substance B is in such a condition that a moderate perturbation of the constituent atoms at its superficies produces no disturbance in the atom-equilibrium of the molecule; whilst in the case of a changeable substance A, the equilibrium of atoms within the molecule is of such a kind that a comparatively unimportant change of motion at the superficies can cause the atoms to assume a different form, that is to say, can cause the production of a different kind of matter. If this be a correct representation of these contact phenomena, then the induced reactions should either be accompanied by a slight heat change, or if accompanied by a considerable heat change, then the reaction should be capable of proceeding by itself in the direction of the heat evolution. An example of the former case is the reaction between hydrogen and iodine; of the latter is the system of hydrogen with oxygen in contact with platinum, which causes a lowering of the reaction-temperature. In conclusion, it is remarked that it is desirable to find a method of research, not only to explain the connection of contact actions with other kinds of chemical change, but also even of the mechanism of the chemical change itself. V. H. V.

Velocity of Saponification. Part II. By L. T. Reicher (*Annalen*, **232**, 103—114; compare Abstr., 1885, 1034).—The author finds that no simple relation exists between the constants of the velocity of saponification of ethereal salts by two different bases. The following table exhibits the results:—

	t.	c (soda).	c' (baryta).	$\frac{c'}{c}$
Methyl acetate.....	9·4	3·493	3·516	1·007
Isoamyl acetate.....	9·4	1·645	1·66	1·009
Ethyl acetate	9·4	2·307	2·144	0·929
Ethyl isovalerate	14·4	0·614	0·597	0·972

The influence of temperature on the velocity of saponification of ethyl acetate by soda is shown by the following numbers:—

t.	*c.*	Calc.
9·4	2·307	2·307
14·4	3·204	3·2
24·22	6·151	6·151
35·14	12·096	11·97
44·94	21·648	21·648

These results agree with Warder's determinations (*Amer. Chem. J.*, **3**, 8). The constant of the velocity of saponification for different temperatures may be calculated by means of the following formula, where T represents the absolute temperature:—

$$\log c = 4{\cdot}53 + 0{\cdot}00754\mathrm{T} - \frac{1780}{\mathrm{T}}.$$

The numbers in the third column are calculated by means of this equation. W. C. W.

Method for Determining Melting and Solidifying Points. By Loviton (*Bull. Soc. Chim.*, **44**, 613—617).—The substance whose melting point is to be observed is placed in a small glass cell in a cylinder piercing a copper box, which is adjusted to the stage of a microscope. The copper box serves as a cooling or heating apparatus, being fitted with tubes, through which hot or cold liquids or vapour may be passed at will by a suitable arrangement of taps, which may be conveniently manipulated whilst observing the substance through the microscope. A small thermometer is placed in contact with the substance, and is so arranged that it may be read whilst working.

Polarised light may be employed with advantage, especially in the examination of butters, for which this method is particularly adapted. A. P.

Oxy-coal-gas Blowpipe and the Zirconia Light. By E. Linnemann (*Monatsh. Chem.*, **6**, 899—908).—A blowpipe for burning oxygen and coal-gas is described. Small discs of zirconia, 15 mm. in diameter, and about 4 mm. thick, are made by pressing very finely powdered zirconia (prepared by heating zirconium chloride) into a steel mortar, about 15 mm. in diameter; they are then heated strongly and fixed on to platinum foil. These may be heated in the oxy-coal-gas flame several hundred times. The zirconia light is very intense, and gives a continuous spectrum. N. H. M.

Drying Apparatus. By V. Meyer (*Ber.*, **19**, 419—420).—Attention is called to the necessity of using perfectly pure liquids in the drying apparatus devised by the author (this vol., p. 278), as otherwise the temperature varies with the size of the flame employed.

Inorganic Chemistry.

The Equations employed by Pebal in his Investigation of Euchlorine. By L. Boltzmann (*Annalen*, **232**, 121—124).—The author points out that the method used by Pebal (this Journal, 1875, 1157), in his investigation on euchlorine, does not prove that euchlorine entirely consists of a mixture of chlorine tetroxide and chlorine. His results do not exclude the possibility that euchlorine may contain a third constituent, O_4. W. C. W.

Continuous Preparation of Oxygen from Bleaching Powder and Cobalt Oxide. By A. Bidet (*Bull. Soc. Chim.*, **45**, 81—83).—A description of a convenient form of apparatus for preparing oxygen gas, in which the gas given off in excess of that actually employed is stored in a reservoir and afterwards used, whilst the generator is being recharged with cobalt oxide. This arrangement is specially adapted for combustions. A. P.

Analysis of Air from Cape Horn. By A. Muntz and E. Aubin (*Compt. rend.*, **102**, 421—423).—The analyses of a series of twenty samples of air collected at Cape Horn during the months of May, July, and August, give a percentage of oxygen varying between 20·97 and 20·72, the mean being 20·864. This number is slightly below the mean of Regnault's analyses, but the difference is very small, and it is evident that the atmosphere at Cape Horn has sensibly the same composition as the atmosphere in other parts of the world. C. H. B.

Action of Nitrites on Ferrous Salts. By A. Piccini and F. M. Zucco (*Gazzetta*, **15**, 475—479).—One of the authors has previously proposed a method of separation of the nitrites from the nitrates, based on the complete decomposition of the former, with evolution of nitric oxide on addition of an excess of ferrous chloride, whilst the nitrate under the same conditions remains unaltered. This reaction is here more minutely examined. On the addition of equimolecular proportions of silver nitrite to ferrous chloride, or preferably of barium nitrite to ferrous sulphate, silver chloride and barium sulphate respectively are precipitated, and the liquid turns brown; finally an ochre-coloured powder separates, accompanied by an evolution of nitric oxide. From quantitative determinations of the nitric oxide evolved the authors consider that ferrous nitrite is at first formed, which decomposes into nitric oxide, ferric oxide, and a basic ferric nitrate, thus: $6Fe(NO_2)_2 = 10NO + Fe_2O_3 + 2Fe_2O_3,N_2O_5$. V. H. V.

Preparation and Titration of Orthophosphoric Acid. By A. Joly (*Compt. rend.*, **102**, 316—318).—In order to prepare phosphoric acid, monammonium phosphate is dissolved in warm concentrated

hydrochloric acid, and the ammonium chloride which separates on cooling is removed by decantation. The liquid is concentrated by evaporation and heated with successive quantities of nitric acid, until all ammonium salts and hydrochloric acid are expelled. Commercial diammonium phosphate may be purified for this purpose by mixing it with hydrochloric acid until the liquid is slightly acid to methyl-orange, and crystallising the monammonium phosphate, which may be further purified by recrystallisation. If arsenic is present (and this element is frequently found in commercial phosphates and phosphorus) it must be removed by the usual methods.

Phosphoric acid can be accurately titrated with alkalis if methyl-orange is used as indicator, but with phenolphthaleïn the end reaction is not sufficiently sharp, and it is still less sharp with soluble blue, C4B (comp. Engel, this vol., p. 420). Arsenic acid gives almost identical results, but in this case the end reaction is not perfectly sharp, even with the methyl orange.

The most accurate method of titrating solutions of phosphoric or arsenic acid is to mix the liquid with phenolphthaleïn, and then gradually to add standard baryta solution, until a gelatinous precipitate forms. This precipitate is a tribarium salt, which rapidly changes into a crystalline dibarium salt. More baryta is carefully added until a gelatinous precipitate is again produced, and this process is continued until a drop of baryta solution produces a permanent intense red coloration. The alteration of the gelatinous precipitate is especially rapid in the case of arsenic.

The author claims priority on the question of the behaviour of various acids with different indicators. C. H. B.

New Mode of Formation of Hypophosphoric Acid and its Ethereal Salts. By A. Sänger (*Annalen*, **232**, 1—42).—*Ethyl hypophosphate* may be conveniently prepared by the action of an excess of ethyl iodide on silver hypophosphate at 100°. It is a colourless liquid of sp. gr. 1·117 at 15°, which decomposes on distillation. It dissolves slowly in cold water, forming ethylhypophosphoric acid and hypophosphoric acid. *Methyl hypophosphate* resembles the ethylic salt. Its sp. gr. at 15° is 1·109. The *propyl*, *isobutyl*, and *amyl hypophosphates* were also prepared. None of these compounds were obtained in the pure state. They all contained silver iodide in solution, which is deposited on the addition of water.

The following salts were prepared by the action of water and a metallic carbonate on alkyl hypophosphates. *Calcium methyl hypophosphate*, $P_2O_6MeHCa + 5H_2O$, and *calcium ethyl hypophosphate*, $P_2O_6EtHCa + 5H_2O$, form yellow needle-shaped crystals. Barium propyl hypophosphate crystallises with 6 mols. H_2O, and calcium isobutyl hypophosphate with 5 mols. H_2O.

Hypophosphoric acid is formed when ammonia and silver nitrate are added to a cold solution of phosphorous acid, but the silver oxide which also results from this reaction oxidises some of the hypophosphoric acid to orthophosphoric acid. The white crystalline precipitate which is produced on the addition of silver nitrate to phosphorous acid has the composition Ag_2HPO_3.

A hydrate of hypophosphoric acid, $H_4P_2O_6 + H_2O$, is obtained in cubical crystals, when the aqueous solution is evaporated over sulphuric acid in a vacuum. The hydrate melts between 79·5° and 81·5°, and decomposes, forming a mixture of phosphoric and phosphorous acids. Attempts to isolate a crystalline hydrate of orthophosphoric acid were unsuccessful, although the existence of a definite hydrate is indicated by the thermic changes which accompany the admixture of orthophosphoric acid with water (comp. Joly, this vol., p. 201).

W. C. W.

Hypophosphoric Acid. By T. Salzer (*Annalen*, **232**, 114—121).—The author finds that an aqueous solution of phosphorous acid does not oxidise on exposure to the air at the ordinary temperature.

Tetrasodic hypophosphate is converted into sodium hydrogen pyrophosphate by bromine, $Na_4P_2O_6 + Br_2 + H_2O = Na_2H_2P_2O_7 + 2NaBr$.

Dimagnesium pyrophosphate, $Mg_2P_2O_6 + 12H_2O$, is obtained as a white, crystalline precipitate by mixing cold solutions of magnesium sulphate and sodium hypophosphate. If hot solutions are used, a gelatinous precipitate is produced, which becomes crystalline after several weeks. If this salt is dissolved in hypophosphoric acid, the *monomagnesium hypophosphate*, $Mg_2H_2P_2O_6 + 4H_2O$, is obtained. It is sparingly soluble in water. Magnesium ammonium hypophosphate appears to be formed when sodium hypophosphate is added to a mixture of magnesium sulphate and ammonium chloride. The *monocalcium salt*, $CaH_2P_2O_6 + 6H_2O$, is obtained by bringing together hypophosphoric acid and the dicalcium salt in exactly their molecular proportions. It crystallises in monoclinic plates. The silver salt, $Ag_4P_2O_6$, obtained by double decomposition, is sparingly soluble in nitric acid, and does not change at 100°.

W. C. W.

Indicators of the Relative Energies of Polybasic Acids. By R. Engel (*Compt. rend.*, **102**, 262—264).—Boric acid, which is neutral to methyl-orange, and very feebly acid to litmus, phenolphthaleïn, and other indicators, is decidedly acid to Poirier's soluble blue, C4B (Abstr., 1885, 931), which even shows the tendency of boric acid to combine with a second equivalent of potash. Borax, which is alkaline to all other indicators, is acid to soluble blue.

Phosphoric acid is monobasic with methyl-orange, bibasic with phenolphthaleïn, and tribasic with soluble blue, but in the latter case the end reaction is gradual. Disodium phosphate is alkaline to litmus and methyl-orange, neutral to phenolphthaleïn, acid to soluble blue. Arsenic acid behaves like phosphoric acid. Phosphorous acid is monobasic with methyl-orange, bibasic with phenolphthaleïn or soluble blue. Hypophosphorous acid shows only a bibasic tendency.

Carbonic acid is bibasic with soluble blue, and alkaline bicarbonates which are alkaline to litmus and methyl-orange can be accurately titrated with potash solution if soluble blue is used as the indicator.

Salicylic and lactic acids are monobasic with all indicators. Parahydroxybenzoic acid is monobasic with litmus, bibasic with soluble blue.

C. H. B.

Germanium, a New Non-metallic Element. By C. Winkler (*Ber.*, **19**, 210—211).—A. Weisbach lately found in the Himmelsfürst Mine, near Freiberg, a mineral which he named argyrodite. Analysis proved this mineral to consist of about 73—75 per cent. of silver, 17—18 per cent. of sulphur, and 0·2 per cent. of mercury, but the analysis always showed a deficiency of 6—7 per cent.

The author has found that this deficiency is due to the presence of a new element, for which he proposes the name Germanium (Ge); this closely resembles antimony, and in acid solutions gives a white *sulphide*, soluble in ammonium sulphide. When argyrodite is heated in a stream of hydrogen, it yields a black crystalline sublimate, which melts to brownish-red drops. This is principally germanium sulphide (mixed with a trace of mercury sulphide); it dissolves in ammonium sulphide, and is reprecipitated by hydrochloric acid as a white powder, readily soluble in ammonia. When heated in a current of air or with nitric acid, the sulphide yields a white *oxide*, which is not volatile at a red heat. This oxide is soluble in potash. The oxide and the sulphide can both be reduced by heating in a current of hydrogen, and yield the element as a grey moderately lustrous substance, which is only volatile (without previous fusion) at a full red heat, and therefore much less so than antimony. The volatilised element is deposited on cooling in small crystals much resembling those of iodine. When germanium or its sulphide is heated in a current of chlorine, the easily volatile white *chloride* is formed, soluble in water.

The author is inclined to consider germanium as the element indicated by the periodic law as probably existing between antimony and bismuth, and is now determining its atomic weight. L. T. T.

Alkaline Hydrates. By E. J. Maumené (*Bull. Soc. Chim.*, **44**, 578—602).—A hydrate of strontium oxide may be obtained in crystals from its aqueous solution, and after drying by the method adopted for the similar barium compound (Abstr., 1883, 1052), has the composition $SrO(H_2O)_{9\cdot583}$; by melting this compound at a low red heat, a second hydrate, $SrO(H_2O)_{0\cdot821}$, is formed.

Potassium oxide forms several definite crystalline hydrates; the first, obtained by allowing a cold aqueous solution of the oxide to crystallise, and drying the rhombic octahedral crystals formed over fused potash, has the composition represented by the formula $K_2O(H_2O)_{5\cdot2}$; a marked reduction of temperature takes place on dissolving this compound in water. A second hydrate, having the composition $K_2O(H_2O)_{3\cdot133}$, may be prepared by pouring a concentrated aqueous solution of potassium oxide, heated to 100°, into a cold porcelain dish; rectangular crystalline plates are formed, these are dried over fused potash; on dissolving in water the hydrate thus obtained, a considerable rise of temperature takes place. By desiccating the hydrate $K_2O(H_2O)_{5\cdot2}$ in a vacuum over fused potash, the hydrate $K_2O(H_2O)_{1\cdot74}$ is formed. This hydrate may also be obtained by fusing potash in a silver dish at a low red heat; by raising the heat to bright redness a fifth hydrate is formed, and may be obtained in crystals by partially cooling the fused mass, and then running off the still liquid hydrate through a hole pierced in the crystalline crust

formed; thus obtained it has the composition $K_2O(H_2O)_{1\cdot205}$; finally, a sixth hydrate was obtained, but not in the crystalline form, by heating potash to a white heat in a platinum dish; it has the composition $K_2O(H_2O)_{0\cdot783}$.

Sodium oxide also forms a series of hydrates; the first,

$$Na_2O(H_2O)_{3\cdot44},$$

crystallises from water in transparent lamellar crystals; by heating this hydrate to a dull redness, a crystalline hydrate, $Na_2O(H_2O)_{1\cdot148}$, is formed, and by further heating to whiteness for about two hours, a third hydrate, $Na_2O(H_2O)_{0\cdot492}$, is obtained.

The author considers that hydroxides of the formula M'HO, or $M''(HO)_2$, never actually exist, a fact foreseen by a theory which he has enunciated; the composition of the hydrates analysed agree almost absolutely with the proportions required by his theory. A. P.

Insolubility of Barium Chloride in Presence of Lithium Chloride. By C. N. Draper (*Chem. News*, **53**, 52).—A crystalline precipitate of barium chloride is obtained when a solution of that salt is added to a concentrated solution of lithium chloride, or to a less marked degree when added to a solution of sodium, potassium, or calcium chloride. D. A. L.

Solubility of Barium Sulphate in Hydrobromic and in Hydriodic Acid. By A. R. Haslam (*Chem. News*, **53**, 87).—When pure barium sulphate is boiled for a quarter of an hour with a solution of pure hydrobromic acid (containing 40 per cent. HBr), it is dissolved to the extent of 1 in 2500 parts of acid solution; with hydriodic acid the solubility is 1 in 6000. D. A. L.

Transference of Copper across a Stratum of Gas. Direct Combination of Nitrogen with Copper. By R. Blondlot (*Compt. rend.*, **102**, 210—212).—The observations recorded in this paper were made in the course of some experiments on the passage of electricity through incandescent gases.

A disc of platinum and a disc of copper, each 33 mm. in diameter, were fixed vertically opposite one another at a distance of 3—4 mm. on two platinum columns, the discs and supports being enclosed in a glazed porcelain globe with an aperture at the bottom. The globe and its contents were heated to bright redness for three hours, and it was found on cooling that the surface of the platinum disc was covered to a depth of 0·1 mm. with a layer of some substance resembling plumbago. This substance was insoluble in cold but soluble in hot nitric acid, yielding a solution which contained copper, whilst a residue of platinum black was left.

In the first experiment the globe was filled with air, and the copper disc was strongly oxidised, but when the discs were heated in an atmosphere of nitrogen, a similar deposit was formed on the platinum, and the surface of the copper, although remaining bright, was distinctly corroded, and showed the internal crystalline structure of the

metal. If, however, the discs were heated in an atmosphere of hydrogen no deposit was formed.

These facts point to the formation of a compound of nitrogen and copper which either combines as a whole with the platinum or is decomposed by it, the copper being deposited. The deposited substance is dissociated and volatilised at a very high temperature.

C. H. B.

Action of Copper on Aqueous Solutions of Sulphurous Anhydride. By CAUSSE (*Bull. Soc. Chim.*, **45**, 3—5).—An aqueous solution of sulphurous anhydride acts slowly on metallic copper, forming cupric sulphite and hyposulphurous acid; if, however, a large excess of sulphurous acid is present, sulphuretted hydrogen is formed, precipitating the cupric sulphite as sulphide and coating the metallic copper with a film of sulphide; a precipitate of sulphur also being formed. These reactions appear to take place more rapidly when the copper is exposed to an atmosphere of moist sulphurous anhydride.

A. P.

Behaviour of Hydrogen Phosphide with some Mercury Salts. By K. A. ASCHAN (*Chem. Zeit.*, **10**, 82; 102—103).—When hydrogen phosphide, prepared by boiling amorphous phosphorus with potash solution (1 : 2 of water), is passed into aqueous mercuric chloride, the precipitate is yellow at first, until all the mercury is precipitated from the solution; it then turns reddish, and by the continued action of the hydrogen phosphide becomes darker, ultimately, after 18 hours, it consists wholly of reduced mercury, whilst the solution contains free hydrochloric acid and some phosphoric acid. In alcoholic solutions, the darker (or brown) stage is more persistent. In the above manner, three compounds of mercuric chloride with mercury phosphide have been isolated, but not pure mercury phosphide. The yellow compound, $3Hg_3P_2,7HgCl_2$, differs from that described by H. Rose ($2PHg_2Cl,HgCl_2 + 3H_2O$, *Ann. Phys. Chem.*, **40**, 78) in being more stable. It can be exposed to air for months without alteration, and can be dried at 105°. At 110—120°, however, it is decomposed, becoming moist and reddish-brown in colour, with separation of globules of mercury. It is decomposed by boiling water.

The red compound, $4Hg_3P_2,5HgCl_2$, is decomposed immediately in the air, but when dried in a current of hydrogen can be kept for a short time. It is decomposed by water. When freshly precipitated, agitation with alcoholic mercuric chloride converts it into the yellow compound.

The brown compound, $Hg_3P_2,HgCl_2$, is decomposed by exposure to air, or in water through which air is being passed. It can, however, be dried in a stream of hydrogen, and is not converted into either of the previous compounds when shaken with mercuric chloride.

The author failed to obtain mercury phosphide by the action of hydrogen phosphide on gently heated mercuric chloride, as described by Rose (*ibid.*, **24**, 335). In solutions of mercuric nitrate, hydrogen phosphide produces at first a white precipitate, which becomes yellow, brown, and grey in succession. These precipitates can be dried and kept in a vacuum. When heated to 140°, the white and yellow compounds explode violently; the grey compound when dry explodes at 94°, or

when moist turns white and explodes at 140°. These compounds likewise explode by percussion; they appear to be mixtures of different compounds of mercury, phosphorus, and nitric acid. Hydrogen phosphide also decomposes mercurous carbonate with the evolution of carbonic anhydride and the formation of an unstable compound, most likely $2PHg_3,6Hg_2O$, readily soluble in nitric acid, and unaltered by dilute sulphuric acid; it becomes brown-red at 120°, and is decomposed at higher temperatures. D. A. L.

Use of Potassium Sulphate in the Fractionation of Rare Earths. By L. DE BOISBAUDRAN (*Compt. rend.*, **102**, 398—399).—The usual method is to saturate with potassium sulphate a greater or less volume of liquid, according to the nature of the earth which it is required to separate. It is, however, difficult to separate in this way the earths which are most soluble in potassium sulphate. The author prefers to add to the somewhat dilute solution a certain quantity of potassium sulphate solution either saturated or non-saturated. Any precipitate of double salt which may form is collected, and the liquid is then fractionally precipitated by the addition of successive quantities of dilute alcohol. C. H. B.

Oxides of Cerium in Practical Use. By J. R. STROHECKER (*J. pr. Chem.* [2], **33**, 260—264; comp. this vol., p. 314).—The varying colours (orange-red to leather colour) of bricks made from the red Hainstadt clay (*loc. cit.*), depend partly on the temperature at which the bricks are burnt; this is shown by the fact that cerium hydroxide (precipitated from a concentrated solution by alkali) when dried and heated acquires a leather colour, whilst orange-red cerium oxide is obtained at a red heat. The lemon colour of bricks made from the clay containing lignite is due to a lower oxide, Ce_3O_4, formed by the reduction of cerium oxide by the carbon present in the clay. These bricks are very rare, but some houses in Frankfort are built of bricks made from the different clays.

It will be possible to obtain brilliant colours for painting from the didymium oxide present in the clays; of which a considerable amount can be got in the preparation of large quantities of cerium oxide. The sky-blue cerium oxide, CeO, is also readily obtained. The oxides of cerium have a further interest with regard to the chemical substitution of isomorphous bases in plants. Their medical properties are being investigated. N. H. M.

Equivalent of Terbia. By L. DE BOISBAUDRAN (*Compt. rend.*, **102**, 395—398) —By fractionation, at first with ammonia and afterwards with potassium sulphate, the author has obtained a specimen of terbia considerably deeper in colour than any which he has previously prepared. This terbia gives the spectra of $Z\alpha$, $Z\beta$, and $Z\gamma$, and contains a small quantity of holmium and minute traces of erbium and samarium. The equivalent of the most deeply coloured fraction was found to be 124·9, and that of the palest fraction 123·8; these values give 163·1 and 161·4 respectively, as the mean atomic weight of the metals contained in the two fractions. These equivalents are con-

siderably higher than those of previously prepared specimens of terbia. Some details respecting the intensities of the spectra of these and three other samples of terbia are given in the original paper.

C. H. B.

Manganites of the Alkaline Earths. By G. Rousseau (*Compt. rend.*, **102**, 425—428).—A mixture of manganese chloride and calcium oxychloride heated for six hours by means of a Bunsen flame (comp. Abstr., 1885, 1114) yields slender, black needles of a trimanganite, $CaO,3MnO_2$, and this result confirms the author's supposition that at low temperatures the manganese oxide becomes polymerised.

Mixtures of manganese chloride with strontium oxychloride yield the manganite when heated at a temperature below 1000° or above 1100°, but between these temperatures the product is a dimanganite, $SrO,2MnO_2$, which is only stable between these limits. Barium behaves in a precisely similar manner, but the phenomena are not so distinct.

On the other hand, if the calcium trimanganite is heated, it gradually decomposes until at a white heat it is converted into a bibasic manganite, $MnO_2,2CaO$. The manganese oxide under the influence of heat undergoes isomeric modifications similar to those observed in the case of certain volatile metallic chlorides.

Strontium dimanganite crystallises in slender, black needles; barium manganite and dimanganite in brilliant, black lamellæ.

C. H. B.

Action of Hydrogen Chloride on Iron. By F. Isambert (*Compt. rend.*, **102**, 423—425).—Hydrogen chloride acts on metallic iron with formation of ferrous chloride and liberation of hydrogen, but hydrogen will also act on ferrous chloride producing the reverse change, and the object of the experiments described in this paper was to ascertain the condition of equilibrium. Dry hydrogen chloride was passed over finely divided iron heated in a porcelain tube to which manometers were attached. The results show that the proportion of hydrogen which is liberated is lower the higher the temperature; for example, the mixture of hydrogen chloride and hydrogen which has no action on iron at a dull red heat, contains 89—91 per cent. of hydrogen, whilst the mixture which has no action at a bright red heat contains only 67—69 per cent. The action of hydrochloric acid, therefore, proceeds in the same way as the action of aqueous vapour, and this result is probably due to the fact that the heat of formation of hydrogen chloride increases as the temperature rises, whilst the heat of formation of ferrous chloride probably varies in the reverse direction. The pressure of the gas seems to be without influence on the results. The ratio of the pressures of hydrogen and hydrogen chloride is constant, whatever the total pressure at a given temperature, a result which is analogous to the law of dissociation.

The iron seems to volatilise and distil from the cold to the warm parts of the tube. The gaseous mixture which removes ferrous chloride at a somewhat low temperature becomes a reducing agent at a higher temperature, and the iron is deposited in the metallic state. This action may take part in the formation of minerals.

C. H. B.

Behaviour of Phosphorus with Iron and Slags. By A. Brackelsberg (*Dingl. polyt. J.*, **258**, 364—370).—In order to determine the behaviour of phosphorus towards iron and slag in the process of reducing iron compounds, a series of trials was made, in which the precipitate obtained by adding ferrous sulphate to sodium phosphate, and consisting of 55 per cent. of ferrous phosphate, 35 per cent. of ferric phosphate, and 10 per cent. of ferric oxide, was heated strongly in a crucible filled with coke. The bright iron regulus obtained was very brittle, and contained 75·45 per cent. of iron and 24·55 per cent. of phosphorus, whilst from the phosphate employed a metal containing 27·4 per cent. of phosphorus should have been obtained. From the results of a further series of experiments, in which slag was added to the charge in the crucible, it is inferred that the presence of slag prevents rather than favours the absorption of phosphorus by iron. This is due probably to the simultaneous presence of silicon in the metal, and the powerful action of silica on the metallic phosphate. It is shown also that sulphur is expelled from iron compounds by phosphorus. On heating a mixture of calcium phosphate (11 parts) and ferric oxide (2·5 parts) with coal, a metal containing 26·4 per cent. of phosphorus was obtained (although it was expected to contain 74 per cent. of phosphorus), so that iron does not appear to absorb more than about 26 per cent. of this element. Brackelsberg concludes that the same results are obtained whether the phosphoric acid is in combination with ferric oxide or lime, a circumstance easily explained by the great affinity which iron has for phosphorus. The iron phosphide (ferro-phosphor) obtained in these trials had a sp. gr. varying between 6·3 and 7·2. It was not very hard, its fracture varied considerably, and it was unaffected by strong mineral acids, aqua regia acting only very slowly, whilst dilute sulphuric acid had no action in the cold. D. B.

Double Potassium and Ammonium Manganese Chromates. By C. Hensgen (*Rec. Trav. Chim.*, **4**, 212—220).—*Potassium manganese chromate*, $K_2CrO_4,2MnCrO_4 + 4H_2O$, is precipitated on mixing solutions of potassium chromate and manganese sulphate, and can be recrystallised from chromic acid solution. It forms blackish-blue, highly refractive crystals, resembling iodine. By varying the proportions of the two salts, substances of intermediate composition are obtained.

The corresponding *ammonium* salt, $(NH_4)_2CrO_4,2MnCrO_4 + 4H_2O$, resembles in appearance the above compound; it decomposes at 200°, and the change is accompanied by a slight explosion when the salt is quickly heated. V. H. V.

Complex Inorganic Acids. By W. Gibbs (*Amer. Chem. J.*, **7**, 313—338; comp. this vol., p. 205).—*Arsenoso-tungstates.*—The alkaline salts are obtained by boiling arsenious oxide with strong solutions of acid tungstates. They are colourless or pale-yellow, and are only easily oxidised in alkaline solution. The following are described:—

$2As_2O_3,18WO_3,7(NH_4)_2O + 18H_2O$, almost colourless prisms;
$As_2O_3,9WO_3,4BaO + 21H_2O$, white, crystalline precipitate;
$8As_2O_3,16WO_3,9Na_2O + 55H_2O$, large, colourless prisms.

Arsenoso-molybdates are obtained in manner similar to the preceding.

$2As_2O_3,8MoO_3,3BaO + 13H_2O$, very pale greenish crystals;
$5As_2O_3,12MoO_3,3(NH_4)_2O + 24H_2O$, colourless crystals;
$3As_2O_3,6MoO_3,2MnO + 6H_2O$, bright orange octahedra.

The zinc and copper salts correspond exactly in composition and form. Another manganese salt, $3As_2O_3,6MoO_3,2MnO + 15H_2O$, is a canary-yellow precipitate.

Phosphoroso-tunystates are readily formed by the action of phosphorous and hydrochloric acids on the higher metatungstates; they are generally better defined than the corresponding phosphoroso-molybdates.

$4H_3PO_3,22WO_3,6(NH_4)_2O + 25H_2O$, crystalline powder;
$16H_3PO_3,32WO_3,5K_2O + 46H_2O$, colourless and crystalline;
$8H_3PO_3,22WO_3,2Na_2O + 35H_2O$, yellow, granular crystals.

Phosphoroso-molybdates.—The preparation of an ammonium salt before described has been repeated, and its composition confirmed, except that the new salt, $4H_3PO_3,24MoO_3,4(NH_4)_2O + 25H_2O$, contains 8 mols. H_2O more.

Antimonoso-tungstates are obtained in manner similar to the arsenoso-compounds; freshly precipitated antimony oxide must be used. The salts of the alkalis are very soluble, forming oily liquids or gummy masses. Addition of barium chloride throws down an indistinctly crystalline salt, $3Sb_2O_3,2BaO,11WO_3 + 18H_2O$.

Antimonoso-molybdates are obtained by boiling antimonious oxychloride with an acid molybdate; a partial reduction of the molybdate always occurs. $3Sb_2O_3,17MoO_3,6(NH_4)_2O + 21H_2O$, forms greenish-yellow, granular crystals. Its preparation is rather uncertain.

Phosphoroso-phospho-tungstates.—The salt, $2H_3PO_3,P_2O_5,24WO_3,5K_2O + 3H_2O$, is obtained by adding potassium bromide to a mixture of phosphorous and orthophosphoric acids and 12 : 5 sodium tungstate.

Phosphoroso-phospho-molybdates.—By adding phosphorous acid to ammonium phosphomolybdate (10 : 2 salt) a greenish-yellow, crystalline precipitate is obtained of the formula

$$2H_3PO_3,3P_2O_5,72MoO_3,9(NH_4)_2O + 38H_2O.$$

Phospho-hypophospho-tungstate, $4P_2O_5,2H_3PO_2,26WO_3,9K_2O,Na_2O + 43H_2O$, is a white, crystalline precipitate.

Arsenoso-phospho-tungstates are obtained by boiling arsenious oxide with a phospho-tungstate, or by adding an orthophosphate to an arsenio-tungstate. $14As_2O_3,3P_2O_5,32WO_3,10K_2O + 28H_2O$, forms minute greenish-yellow crystals; $2As_2O_3,2P_2O_5,12WO_3,5K_2O,Na_2O + 15H_2O$, a yellow oil, drying to a pale-yellow, gummy, transparent mass; $As_2O_3,4P_2O_5,60WO_3,7K_2O + 55H_2O$, pale-yellow crystals.

Arsenoso-arsenio-tungstates are formed in manner similar to the preceding salts. $As_2O_3,4As_2O_5,21WO_3,10K_2O + 26H_2O$, forms a white crystalline precipitate. H. B.

Crystals of Thorium. By W. C. Brögger (*Jahrb. f. Min.*, 1886, **1**, Ref., 25—26).—The metal prepared by L. F. Nilson (Abstr., 1883,

152, 553) was a fine grey powder. The separate grains, only 0·0001 to 0·0002 gram in weight, prove to be thin bent plates produced from the regular and irregular growth of numberless small tabular hexagonal crystals, each apparently exhibiting a combination of two rhombohedra with the basal plane. From the angular measurements, however, it would seem probable that the crystals of thorium are regular, and exhibit a combination of the octahedron and cube. This view is supported by the nature of the twin crystals, the plane of twinning being an octahedral plane. B. H. B.

Extraction of Vanadium from Magnetite; the Behaviour of several Vanadium Compounds towards Reagents; the Quantitative Determination of Vanadium and its Separation from Chromium. By E. Claassen (*Amer. Chem. J.*, **7**, 349—353).—Magnetite is treated with hydrochloric acid; the residue is decomposed by igniting with nitre and soda. The two portions are then mixed, more nitre and sodium carbonate added, and the whole fused; the aqueous solution of the fused mass contains all the vanadium and chromium.

Vanadium oxide is not entirely soluble in ammonium sulphide. By igniting it with sulphur and sodium carbonate a mass is obtained soluble in water. The whole of the vanadium cannot be precipitated from such a solution by treatment with an acid.

Before precipitating a solution of a vanadate with ammonium chloride it must be made slightly alkaline with ammonia; the filtrate from the ammonium metavanadate should be precipitated by alcohol, when a small additional amount of metavanadate is obtained.

Lead vanadate may be decomposed by hydrochloric acid and alcohol. Barium vanadate is not entirely decomposed by dilute sulphuric acid, but is by ignition with potassium pyrosulphate. A solution containing a hypovanadate is not completely precipitated by mercuric chloride and ammonia.

A mixture of vanadium and chromium oxides may be separated by fusion with sulphur and sodium carbonate; the chromium remains as oxide; the vanadium goes into solution as a sulpho-salt. H. B.

Solubility of Antimonic Oxide in an Alkaline Solution of Glycerol, and a New Mordant for Cotton Dyeing. By H. Köhler (*Dingl. polyt. J.*, **258**, 520—525).—It has been shown by Morawsky, Puls, and Schottländer that different metallic oxides are dissolved by alkaline solutions of glycerol, such as the oxides of iron, manganese, copper, and bismuth. The author finds that antimonic oxide behaves in a similar manner. It was proved by experiment that the solubility of the oxide depends on the presence of glycerol and not on the alkali employed. The alkalinity of the solution, however, influences the solubility of the oxide, the ratio increasing until a compound is obtained consisting of equal molecular weights of caustic soda, glycerol, and oxide. Caustic potash gave less favourable results, whilst ammonia does not dissolve even a trace of the metallic oxide.

The solution of sodio-antimonic glyceride has a strongly alkaline reaction, and may be saturated with an acid to a certain limit, but beyond

this, antimonic oxide separates in the form of a thick precipitate soluble in an excess of the acid. When exposed to the action of the atmosphere, the solution becomes turbid, and deposits a white mass of microscopic crystals which are insoluble in water, and correspond in composition with the formula $Na_4Sb_2O_7$. The solution of sodio-antimonic glyceride can be used with advantage as a mordanting agent in dyeing. Care should, however, be taken to remove antimony sulphide, almost invariably present in commercial antimonic oxide, otherwise red antimony sulphide will be deposited on the fibre by the tannin, leading to the production of colours lacking in brightness and intensity. D. B.

Antimony Sulphide. By A. Ditte (*Compt. rend.*, **102**, 212—214).—The double sulphides of antimony and potassium previously described (this vol., p. 309), can also be obtained from anhydrous antimony sulphide, if it is finely powdered and digested with a concentrated solution of the alkaline sulphide. A highly concentrated solution deposits yellow needles of the composition $K_2S,2Sb_2S_3$; a moderately concentrated solution at first deposits the same compound, and afterwards $2K_2S,Sb_2S_3$.

The conditions of equilibrium between antimony sulphide, antimony chloride, hydrogen sulphide, and hydrogen chloride (see Berthelot, this vol., p. 308), are materially modified by changes of temperature. If the liquid is heated, the hydrates of hydrogen chloride are more easily dissociated, whilst at the same time less and less hydrogen sulphide remains dissolved in the liquid, and a point is eventually reached at which hydrated antimony sulphide can no longer exist, and crystals of the anhydrous sulphide are formed. This is well seen when the hydrated sulphide is boiled with moderately dilute hydrochloric acid. At first there is only a slight evolution of hydrogen sulphide, but as the liquid evaporates and the solution becomes more concentrated, decomposition of the antimony sulphide takes place more rapidly, and at a certain temperature the action of the dissolved hydrogen sulphide on the antimony chloride also in solution produces anhydrous antimony sulphide, which separates in shining grey needles. If the boiling is continued, the hydrated sulphide is still more easily attacked, whilst the reverse action produces only the anhydrous sulphide, until at last the whole of the antimony sulphide remaining undissolved is converted into grey anhydrous needles with a metallic lustre. The formation of the grey crystals begins when the solution contains about 54 grams of anhydrous hydrogen chloride per litre, a part being in the state of antimony chloride.

Hydrated antimony sulphide is not attacked by sulphuric acid unless the latter is concentrated and boiling, but the phenomena are strictly analogous to those observed in the case of hydrochloric acid.

The sp. gr. of natural grey antimony sulphide is 4·6—4·7; that of the fused sulphide obtained by the direct union of sulphur and antimony, 4·892; that of the anhydrous sulphide prepared in the wet way, 5·012. The mean sp. gr. of the sulphide calculated from the sp. gr. of its constituents is 3·982 or 4·095, according as the

sp. gr. of sulphur is taken as 1·97 or 2·07. The formation of antimony sulphide is therefore accompanied by considerable contraction, and this fact corresponds with its high heat of formation.

Fuchs stated that if the sulphide is fused and poured into water, its sp. gr. diminishes, and the cooled amorphous substance yields an orange-red powder. The author finds that when the antimony sulphide is treated in this way its sp. gr. does diminish, but it yields a black powder similar to that of the ordinary compound.

Hydrated antimony sulphide after prolonged drying over sulphuric acid has the composition $Sb_2S_3 + 2H_2O$. If heated above 100°, it loses water, and acquires a metallic grey colour. C. H. B.

New Solvents of Anhydrous Auric Chloride. By L. Lindet (*Bull. Soc. Chim.*, **45**, 149—151).—Anhydrous auric chloride dissolves in arsenious chloride (22 per cent. dissolving at 160° and 2·5 per cent. at 15°), and is soluble to a similar extent in antimonic chloride. It also dissolves in stannous and titanous chlorides, but is much less soluble, only 4 per cent. being dissolved at 150°. Silicon tetrachloride dissolves only a trace, even at a high temperature. It crystallises from these solvents in triclinic prisms of a fine dark-red colour.

A. P.

Mineralogical Chemistry.

Occurrence of Sulphur on the Island of Saba. By G. Lunge (*Dingl. polyt. J.*, **259**, 43—45).—Saba (one of the Antilles belonging to Holland) is rich in sulphur beds, but the working of the mines is attended with great difficulties, owing to the heavy rains and the frequency of hurricanes. In some parts of the mines, the rock contains as much as 93 per cent. of sulphur; the average amount does not, however, exceed 45 per cent. D. B.

Embolite from Australia. By J. M. H. Munro (*Chem. News*, **53**, 99).—The sample analysed came from St. Arnaud, Victoria, and was found disseminated throughout a specimen of ferruginous quartz in form of minute, irregular nodules. Its composition was: Ag 64·45, Br 25·84, Cl 9·70, which agrees substantially with the composition AgCl,AgBr, already suggested by Wood. D. A. L.

Crystalline System of Cryolite. By Des Cloizeaux (*Jahrb. f. Min.*, 1886, **1**, Ref., 16—17).—Since Krenner and Groth came to the conclusion that cryolite was monoclinic, and not triclinic as stated by Websky and Des Cloizeaux, the latter has repeated his observations on two good crystals. All his results support the view that cryolite is triclinic; the best evidence being the results of the observations in parallel light. B. H. B.

Occurrence of Cryolite in Greenland. By P. Johnstrup (*Jahrb. f. Min.*, 1886, **1**, Ref., 28—31).—The principal rock occurring at the Arsuktjord, on which Ivigtuk is situated, is grey gneiss. At the Arsuk Island, it passes into mica-schist, clay-slate, and quartzite. The gneiss is traversed by veins of diabase and syenite. The cryolite at Ivigtuk is enclosed in an irregular eruptive mass of granite. There are two masses of cryolite. The central one is 500 feet long and 100 feet broad, and consists for the most part of cryolite; quartz, spathic iron ore, galena, iron pyrites, zinc blende, copper pyrites, and wolfram being irregularly distributed through the mass. In the peripheral mass of cryolite, which envelopes the central mass, the predominating minerals are quartz, microcline, and ivigtite, together with fluorspar, cassiterite, molybdenite, arsenical pyrites, columbite, and the minerals which occur in the central mass. This belt has a thickness of 100 feet.

Two varieties of cryolite occur—the original compact cryolite, and the secondary variety crystallised in fissures. The former is generally white, but is sometimes black; the proportion of organic matter being less than 0·1 per cent. The crystallised variety is perfectly colourless, and exhibits a conchoidal fracture. Cryolite is easily acted on by the atmosphere, and dissolved. One part is soluble in 2730 parts of water at 12°; a saturated aqueous solution thus containing 0·04 per cent. of cryolite. Where the cryolite is dissolved more or less completely, thomsenolite and ralstonite occur as secondary minerals; ralstonite being formed subsequently to thomsenolite. Knop's pachnolite is merely thomsenolite in acicular crystals. B. H. B.

Minerals from Chile and Bolivia. By F. Sandberger (*Jahrb. f. Min.*, 1886, **1**, Mem., 89—91).—Guejarite, a mineral hitherto only known to occur in Spain, has been discovered by the author in a sample of ore from Machacamara in Bolivia. Bournonite is of frequent occurrence in Chile and Bolivia, and in many places products of its alteration are met with, for instance, linarite, lead antimonate and sulphate, from the Palastina mine at Antofagasta.

In conclusion, the author mentions a crystallised product from the Antofagasta silver-works. This is antimony-nickel. The substance, which is exactly like the mineral in form and colour, occurs as a thin coating in fissures in the hard lead found in 1880 in the bed of a blast furnace. B. H. B.

Pseudomorphs of Calcite after Aragonite. By M. Bauer (*Jahrb. f. Min.*, 1886, **1**, Mem., 62—80).—From an investigation of the nature of the pseudomorphs of calcite after aragonite, recently discovered at Klein-Sachsenheim in Würtemburg, the author concludes that all pseudomorphs of calcite after aragonite are not to be regarded as paramorphs produced by molecular rearrangement without losing or taking up substances, but should rather be classed with pseudomorphs by alteration. This theory holds good for all calcite pseudomorphs which have a coating of brown-spar, and especially for those of a spongy character, which contain cavities between the recently formed calcite crystals. B. H. B.

Manganese-Apatite from Saxony. By F. Sandberger (*Jahrb. f. Min.*, **1**, Mem., 89). The discovery of manganese-apatite in Europe was announced by Hilger (*Jahrb. f. Min.*, 1884, **1**, 171), who found it in the pegmatite of Zwiesel in Bavaria. The author has now obtained it from a second German locality: Penig in Saxony, where it also occurs in pegmatite. B. H. B.

Szaboite. By J. A. Krenner and F. Koch (*Jahrb. f. Min.*, 1886, **1**, Ref., 23—24).—The szaboite from the Aranyer Mountain, described by G. A. Koch (Abstr., 1879, 441) as triclinic, is hypersthene, according to the observations of Krenner. The forms observed were: $\infty P\bar{\infty}$, $\infty P\breve{\infty}$, ∞P, $\frac{1}{2}P$, $P\bar{2}$, $0P$; $a : b : c = 0{\cdot}9668 : 1 : 1{\cdot}1473$. An analysis of weathered szaboite by F. Koch gave:—

SiO_2.	MgO.	FeO.	Fe_2O_3.	CaO.	Ignition.	Total.
51·681	22·824	8·465	12·687	3·093	0·960	99·710

The percentage of FeO in the unaltered substance was found to be 19·702. B. H. B.

Minerals new to Britain. By M. F. Heddle (*Min. Mag.*, **5**, 1—31; *Jahrb. f. Min.*, 1886, **1**, Ref., 17—23). The author announces the occurrence of a number of minerals not before noticed as occurring in Britain. The minerals are: 1. Halloysite from the Hospital Quarry, near Elgin; 2. Fibrolite from Pressendye Hill, in Aberdeenshire; 3. Martite from Bute; 4. Turgite from the Island of Kerrera, in Argyllshire, and from Oban; 5. Xonaltite from Kilfinnichan, Mull.

The occurrence, as British species, of the following rocks and minerals has been before noted, but no analyses of these have hitherto been published. Analyses are given of: 1. Schiller spar from Aberdeen; 2. Hydrous saussurite from Lendalfoot in Ayrshire; 3. Tachylite from Quiraing, in Skye; 4. The dolerite from the same locality; 5. Pitchstone from Corrieghil, Arran; 6. Spherulite from Corrieghil, Arran; 7. Paulite from Craig Buroch, Banffshire; 8. Zoisite from Gartally, in Glen Urquhart, and from Durham Bridge, Inverness-shire; 9. Idocrase from Dalnabo, Aberdeenshire; 10. Andalusite from Clashnaree in Clova, and from the Mill of Auchintoul, Marnoch, Banffshire; 11. Withamite from Glencoe; 12. Olivine from columnar basalt at Shooter's Point, Elie, Fife, and from the summit of Halival; 13. Pinite from the Burn of Craig, Aberdeenshire; 14. Gigantolite from Torry, Aberdeen; 15. Chlorophyllite from the Burn of Craig; 16. Scapolite from Glen Urquhart, and from the Tiree marble; 17. Pyrrhotite from Fiermore, Blair Athol; 18. Pyromorphite (so-called chromo-phosphate of lead variety) from Leadhills; 19. Aragonite from Leadhills; 20. Reddle from Newton Quarry, near Elgin; 21. Lydian stone from Kinkell, Fife; 22. Hornstone from Blackford Hill, Edinburghshire; 23. Chert from the Fee Donalt mine, at Strontian; 24. Lignite from a bed under the "Organ" at the Giant's Causeway; 25. Ozokerite from Binny Quarry, Linlithgowshire. B. H. B.

Peridotites near Peekskill, New York. By G. H. Williams (*Amer. J. Sci.*, **31**, 26—41).—The author gives a petrographical

description of the most basic members of the interesting group of massive rocks, designated by J. D. Dana as the "Cortland Series," on the Hudson River, about 40 miles north of the city of New York. The author proposes to describe petrographically the different types of this series in succession. In the present paper only such rocks are described as contain olivine. They are, for the most part, destitute of any considerable quantity of felspar, and belong, therefore, to the family of peridotites. They are described in detail by the author under the heads of (1) hornblende-peridotite, and (2) augite-peridotite. B. H. B.

Nephelinic Tephrite in the Valley of the Jamma. By A. M. Levy (*Compt. rend.*, **102**, 451—453).—A nephelinic tephrite passing into phonolite occurs in the form of a thick dyke, amongst rocks of the middle jurassic age, on the left bank of the Jamma, a tributary of the Blue Nile, in the kingdom of Choa. The rock has a greyish colour, and a saccharo-crystalline fracture. The crystals of the first consolidation consist exclusively of somewhat rare *débris* of crystals of orthose; but the crystals of the second consolidation include microliths of nepheline, orthose, oligoclase, and amphibole.

The nepheline constitutes about one-fifth of the rock, and occurs in small hexagonal prisms with a negative optical axis. They contain inclusions of oligoclase and gas bubbles arranged along the zones of growth of the crystals.

The oligoclase occurs in slender microliths resembling those of micaceous porphyry. The amphibole shows green polychroism, and occurs in very elongated crystals grouped in radiating bundles. Certain parts of the rock contain granular quartz associated with oligoclase.

The rock is not very homogeneous, and its constituents are somewhat irrgeularly distributed, the individual minerals being more or less aggregated in different parts. It shows no flow-structure, and the elements of the second crystallisation must have developed after injection, during a period of rest which allowed of a partial liquation of the fused magma. C. H. B.

Meteorite from Green Co., Tennessee. By W. P. Blake (*Amer. J. Sci.*, **31**, 41—46).—This meteoric iron was found completely buried in the earth, and there is no record of the time of its fall. The weight of the mass is 290 lbs., equivalent to 131·82 kilos.* The original weight is said to have been 300 lbs. The form of this iron is very curious, being an extremely regular long ellipsoid, tapering at each end to a flattened point. The surface is scaly and rusty, but is in general smooth and evenly curved, with the exception of several cup-shaped depressions, due, apparently, to unequal exfoliation. The meteorite clearly belongs to the class of exfoliating, deliquescent irons, several examples of which have been found in Tennessee.

For the examination of the internal structure, a slice was cut from one end. The sp. gr. of the iron was found to be 7·858. Analysis

* 639·36 kilos. in the original paper.

showed the presence of iron, nickel, and chlorine; a quantitative determination of the iron and nickel giving the following results:—

Fe.	Ni.	Total.
91·421	7·955	99·376

On dissolving the iron in pure cold nitric acid, a grey heavy metallic powder was thrown down. In composition, it is an alloy of nickel and iron, the nickel preponderating. B. H. B.

Organic Chemistry.

Action of Inorganic Iodides on Organic Chlorides and Bromides. By H. SPINDLER (*Annalen*, **231**, 257—285).—The iodides of the paraffin series may be conveniently prepared from the corresponding bromides and chlorides by the following method. The theoretical quantity of calcium iodide (fused in its water of crystallisation) and the organic compound are brought into a glass tube, from which the air is exhausted before it is sealed at the blowpipe. If the organic compound is liquid, it is introduced into the tube in a thin glass bulb. The presence of moisture other than the water of crystallisation of the calcium iodide must be carefully avoided. The tubes are heated at 60—65° for 120 hours.

	Product.	Per cent.
Monochlorobenzene, PhCl	—	0
Methylene chloride, CH_2Cl_2	CH_2I_2	63·38
Chloroform, $CHCl_3$	CHI_3	17·4
Carbon tetrachloride, CCl_4	CI_4	14·44
Ethylene chloride, $C_2H_4Cl_2$	$C_2H_4I_2$	86·25
Ethylidene chloride, $CH_3{\cdot}CHCl_2$	$CH_3{\cdot}CHI_2$	40·6
Monochlorethylene chloride, $CH_2Cl{\cdot}CHCl_2$	Not determined	7·29
Tetrachlorethane, $CHCl_2{\cdot}CHCl_2$	„	1·32
Pentachlorethane, C_2HCl_5	„	1·72
Hexachlorethane, C_2Cl_6	—	0
Normal propyl bromide, $Pr^{\alpha}Br$	$Pr^{\alpha}I$	76·65
Isopropyl bromide, $Pr^{\beta}Br$	$Pr^{\beta}I$	82·06
Allyl chloride, C_3H_5Cl	C_3H_5I	96·29
β-Dichlorhydrin / Trichlorhydrin	Complete decomposition	—
Acetic chloride, $C_2H_3O{\cdot}Cl$	C_2H_3OI	39·26
Ethyl Monochloracetate, $CH_2Cl{\cdot}COOEt$	$C_2H_2IO_2Et$	93·05
Ethyl Dichloracetate, $CHCl_2{\cdot}COOEt$	$C_2HI_2O_2Et$	91·92
Monochloracetic chloride	Complete decomposition.	
Ethylene chlorobromide, $CH_2Cl{\cdot}CH_2Br$	$CH_2I{\cdot}CH_2I$	92·96
Ethylidene chlorobromide, $CH_3{\cdot}CHClBr$	$CH_3{\cdot}CHI_2$	62·22
Chloral	Decomposition	—
Chloropicrin, $CCl_3(NO_2)$	Decomposition	—
Dichlorodinitromethane, $CCl_2(NO_2)_2$	Decomposition	—

The table (p. 434) shows the percentage of chloride or bromide converted into iodide. W. C. W.

Action of the Aluminium Halogen Compounds on the Halogen-derivatives of the Paraffins. By C. Kerez (*Annalen*, **231**, 285—307).—The following are the results of a long series of experiments on the action of aluminium chloride, bromide, and iodide on propyl chloride and iodide. Propane is formed by the action of aluminium chloride on propyl iodide at temperatures between 110° and 168°, but the yield never exceeds 75 per cent. of the theoretical. By the prolonged action of the chloride at the ordinary temperature, propylene is produced.

Aluminium chloride and propyl chloride, aluminium bromide, and propyl chloride or iodide, and aluminium iodide and propyl chloride at temperatures ranging from 118° to 140° yield propylene. No propane is formed in any of these reactions. W. C. W.

Carbamincyanamide. By A. Wunderlich (*Ber.*, **19**, 448—456).—The author cites many reasons for regarding Hallwach's amidodicyanic acid (*Annalen*, **153**, 293) as carbamincyanamide,

$$CN{\cdot}NH{\cdot}CONH_2.$$

By the action of sodium cyanamide on ethereal carbimides and thiocarbimides, the corresponding replaced sodium carbamincyanamides are obtained. These substances are neutral in reaction; the thio-compounds crystallise well, but, unlike those free from sulphur, do not yield crystalline copper-derivatives; when treated with acids, these compounds yield the crystalline carbamincyanamides, of which the following have been prepared:—Methylthiocarbamin-ethylcyanamide, CN·NEt·CS·NHMe, melting at 106°; ethylthiocarbaminmethylcyanamide, CN·NMe·CS·NHEt, melting at 162°; allylthiocarbaminmethylcyanamide, $C_6H_9N_3S$, melting at 110°; phenylthiocarbaminethylcyanamide, melting at 119°; and carbaminethylcyanamide, CN·NH·CO·NHEt, melting at 121°.

When these thio-compounds are boiled with ammonium sulphide, they yield the corresponding dithiobiurets, which are readily soluble in alkalis and ammonia; those containing fatty radicles are soluble in hot water, but nearly insoluble in ether; whilst the phenyl-derivative dissolves readily in hot alcohol and ether, but is insoluble in water.

Monothiobiuret, $C_2H_5N_3OS$, is prepared by boiling carbamincyanamide with ammonium sulphide; it crystallises in needles containing 1 mol. H_2O. A. J. G.

Melanurenic Acid. By M. Striegler (*J. pr. Chem.* [2], **33**, 161—180).—Melanurenic acid, $C_6N_8H_8O_4$, is prepared by gradually adding 300 grams of sulphuric acid to 109 grams of melam; a considerable rise of temperature takes place. The whole is then heated for five minutes at about 190°. When cold, the liquid slowly deposits crystals of melanurenic acid sulphate; these are filtered, washed, and whilst still moist rubbed to a fine paste, then dissolved

in boiling ammonia and filtered. The solution yields the acid in splendid, lustrous needles which change to a white, chalky powder, when dried at 100°. The yield is 40 per cent. of the weight of melam. The *normal sodium salt*, $C_6H_8H_6Na_2O_4 + 6H_2O$, is a crystalline substance, rather readily soluble in water; the *hydrogen sodium salt*, $C_6N_8H_7NaO_4 + 5H_2O$, is best prepared by the action of carbonic anhydride on a solution of the normal salt. The amount of water of crystallisation varies. The *normal potassium salt* forms yellowish aggregates of rhombic pyramids; the *hydrogen potassium salt* crystallises in groups of slender needles; the *normal* and *acid ammonium salts*, with 5 and $6\frac{1}{2}$ mols. H_2O respectively, the *calcium*, *barium*, *silver*, and other salts are also described. They are more stable than the salts which melanurenic acid forms with acids.

Phosphorus pentachloride reacts with melanurenic acid with formation of cyanuric chloride. N. H. M.

Composition of Brandy from Wine. By C. Ordonneau (*Compt. rend.*, **102**, 217—219). — Careful fractional distillation of Cognac brandy 25 years old showed the presence of the following substances, the quantities being given in grams per hectolitre of brandy: aldehyde, 3; ethyl acetate, 35; acetal, traces; normal propyl alcohol, 40; normal butyl alcohol, 218·6; amyl alcohol, 83·8; hexyl alcohol, 0·6; heptyl alcohol, 1·5; propionic, butyric, and caproic ethers, 3; œnanthylic ether, about 4; amines, traces. The presence of normal butyl alcohol and amyl alcohol in such large proportion is especially important.

Similar treatment of commercial alcohols from maize, beetroot, and potatoes showed that they contain, besides other substances, propyl alcohol, active and inactive amyl alcohol, pyridine, a base which seemed to be collidine, and isobutylic alcohol, without any traces of normal butyl alcohol.

These results indicate that the difference in flavour between brandy from wine and the alcohol of the distilleries, is due to the fact that the former contains normal butyl alcohol, whilst the latter contains isobutyl alcohol, which has a disagreeable taste. It seemed probable that the normal alcohol is a product of fermentation under the influence of elliptical yeast, whilst the iso-alcohol is a product of fermentation by beer yeast, and this supposition is confirmed by experiment. A quantity of molasses was fermented by means of yeast from wine, and from the product the author distilled a spirit which contained normal butyl alcohol, together with amyl alcohol, and closely resembled in flavour and odour the spirit obtained by the distillation of new wines.

It follows from these results that in order that the alcohol of the distilleries may have the pleasant aroma and flavour of wine brandy, instead of the usual disagreeable flavour, the molasses, &c., should be fermented with elliptical or wine yeast, instead of with ordinary beer yeast. This fermentation can be easily accomplished, and proceeds rapidly at 28—32°.

The true wine bouquet of wine brandies and wines is due to a substance which is present only in small quantity, and seems to be a

terpene boiling at 178°. Its products of oxidation give to old brandy its characteristic properties.

The amines which exist in brandy in small quantity probably belong to the pyridine series. C. H. B.

Action of Methyl Iodide and Zinc on Butyrone: Synthesis of Methyl Dipropyl Carbinol. By A. Gortaloff and A. Saytzeff (*J. pr. Chem.* [2], **33**, 202—207).—*Methyl dipropyl carbinol*, $CMePr_2{\cdot}OH$, is prepared by the action of butyrone (1 mol.) on methyl iodide (3 mols.) in presence of zinc in a manner similar to ethyl dipropyl carbinol (next Abstract). It is a colourless liquid having an odour resembling that of the ethyl compound (*loc. cit.*), and boils at 161·5° (corr.). Sp. gr. at 20° = 0·82479 (water at 20° = 1). It is readily soluble in alcohol and ether, almost insoluble in water. The *acetate*, $CMePr_2{\cdot}OAc$, is a colourless liquid boiling at 174—176°. Sp. gr. at 20° = 0·8588 (compared with water at 20°). On oxidation, methyl dipropyl carbinol yields acetic and propionic acids, together with small quantities of butyric acid and carbonic anhydride. N. H. M.

Action of Ethyl Iodide and Zinc on Butyrone: Synthesis of Ethyl Dipropyl Carbinol. By A. Tschebotareff and A. Saytzeff (*J. pr. Chem.* [2], **33**, 193—202).—*Ethyl dipropyl carbinol*, $CEtPr_2{\cdot}OH$, is prepared by the action of 70 grams of butyrone on 287 grams of ethyl iodide in presence of as much zinc as is just covered by the liquid. After some days, the mixture, which has become thick, is stirred and warmed slightly on a water-bath. The product is then poured on to water and ice, treated with sulphuric acid, and distilled. The oil thus obtained is separated from the water, dried, and redistilled. It is a transparent liquid with a slight odour resembling that of the higher saturated alcohols, and boils at 179·5° (corr.). Sp. gr. at 20° = 0·83492, compared with water at 20°. It is almost insoluble in water, soluble in all proportions in alcohol and ether. The *acetate*, $CEtPr_2{\cdot}OAc$, is formed when the carbinol is heated with acetic anhydride for 12 hours at 140°. It is a colourless liquid boiling at 188—192°, and has an odour resembling that of the alcohol. Sp. gr. at 20° = 0·8697, compared with water at 20°.

When ethyl dipropyl carbinol is oxidised with chromic mixture, it is converted into acetic, propionic, and butyric acids with evolution of carbonic anhydride. N. H. M.

Specific Gravity and Index of Refraction of Ethyl Ether. By A. C. Oudemans (*Rec. Trav. Chim.*, **4**, 269—285).—In this paper the results are given of determinations of specimens of ether, purified in the usual way, and finally distilled over sodium in a vacuum.

From these results, various empirical equations are deduced to express the volume of ether in terms of temperature according to the equation $V_t = V^\circ (1 + ab + bt^2 + ct^3)$, if the corrected density at 0° be taken as 0·7359. The results are in accordance with the former observations of Muncke, Pierre, and Kopp.

Determinations are also given of the indices of refraction for the lines K_α, Li_α, H_α, Na_α, Ca_β, Tl_ϵ, H_β, Sr_δ, H_γ, and Rb_α; and from these

the specific refractive powers are calculated according to the formulæ of Landolt and Lorentz.

From the figures given for ether and other substances in a series of tables, it is shown that the purely empirical formula of Landolt leads to nearly constant values with variation of temperature, whilst those from Lorentz' formula are not so constant. V. H. V.

Maltodextrin. By H. T. Brown (*Ber.*, **19**, 433—435).—A reply to Herzfeld (this vol., p. 221).

Levulose. By A. Herzfeld and H. Winter (*Ber.*, **19**, 390—394).—It has recently been shown by Herzfeld and Börnstein (this vol., p. 328) that trihydroxybutyric acid is formed by the oxidation of levulose with mercuric oxide; in this paper, details of experiments are given to show that the same acid is formed in small quantities by the oxidation of levulose with bromine. The acid is dextrorotatory, but the value for $[\alpha]_D$ has not yet been determined.

In order to examine the discrepancy between the observed value for the specific rotatory power of crystalline levulose, $[\alpha]_D = -69{\cdot}24$, $p = 9$, and that calculated, $[\alpha]_D = -90{\cdot}18$, from the specific rotatory power of invert sugar, the authors have carefully prepared samples of crystalline levulose dried over phosphoric anhydride. It is found that the substance obtained by crystallisation from absolute alcohol has the composition $C_6H_{12}O_6$, and a specific rotatory power $[\alpha]_D = -71{\cdot}4$, $p = 20$. As the specific rotatory power of levulose from invert sugar is $[\alpha]_D = -40{\cdot}18$, it may be considered probable either that dextrose and levulose cannot be perfectly separated by absolute alcohol, or that the invert sugar contains a glucose of less lævorotatory power than levulose. V. H. V.

Cyanhydrin of Levulose. By H. Kiliani (*Ber.*, **19**, 221—227).—This cyanhydrin (this vol., p. 219) crystallises from water in tabular, monoclinic crystals of melting point 110—115°. It has an exceedingly slight dextrorotatory power. Neither an amine nor amide could be obtained from it. Metallic hydroxides readily resolve it into hydrocyanic acid and levulose.

The author has prepared *methylbutylacetic acid* by means of the acetoacetic reaction, and finds that it is identical with the acid previously described (*loc. cit.*), as obtained by the reduction of the lactone produced by saponification of the cyanhydrin with hydrochloric acid. It boils at 210° (corr.), and gives a *calcium salt* crystallising with $6H_2O$, and a *strontium salt* with $5H_2O$. The characteristics of ethylpropylacetic acid (this vol., p. 441) are quite distinct.

L. T. T.

Action of Alcoholic Chlorides on Ammonia and the Methylamines. By C. Vincent and Chappuis (*Compt. rend.*, **102**, 436—438).—Carefully measured volumes of the gases were liquefied by pressure in a Cailletet's apparatus, and allowed to react under these conditions at a low temperature. Methyl chloride and ammonia yield ammonium chloride, which is formed in largest quantity, and the chlorides of monomethylamine and trimethylamine. If methyl or

ethyl alcohol is saturated with the two gases in the cold, ammonium chloride is still the principal product, and is deposited in large transparent crystals, but the other product is tetramethylammonium chloride, no trimethylamine being formed.

Methyl chloride and monomethylamine yield only the chlorides of monomethylamine and tetramethylammonium, no ammonium chloride being formed. Methyl chloride and dimethylamine yield only the chlorides of dimethylamine and tetramethylammonium.

Methyl chloride and trimethylamine yield only tetramethylammonium chloride, and the reaction is accompanied by considerable development of heat.

Liquefied ethyl chloride has no action on liquefied ammonia either in the cold or at the critical point, even in presence of a small quantity of alcohol, and the two compounds react very slowly in alcoholic solution under ordinary pressure. Ethyl chloride is also without action on trimethylamine under the above conditions.

Propyl chloride reacts extremely slowly with ammonia in alcoholic solution, there being no crystalline deposit even after several weeks.

C. H. B.

Specific Heats and Specific Gravities of Acids of the Acetic Series. By C. Lüdeking (*Ann. Phys. Chem.* [2], **27**, 72—80).—As the physical constants of the lower members of the acids of the acetic series are in many respects anomalous, it seemed desirable to make a series of determinations of the specific gravities, the specific heats, and the heats of hydration of these acids, with a view of deciding whether simple gaseous molecules, $C_nH_{2n}O_2$, are not combined in the liquid state into more complex groupings, $m(C_nH_{2n}O_2)$, which are dissociated into their components under certain conditions. The results, however, show that these various physical properties are correlated with the concentration. Thus the curve representing the specific gravities of solutions of formic, acetic, propionic, and butyric acids in terms of concentration attain maxima points, which correspond to a definite proportion of molecules of acid with molecules of water; from these points, the curve falls at first slowly, and then gradually so as to become approximately asymptotic to the axis of the abscissæ.

Precisely similar phenomena are observable in the results obtained for the specific heats of mixtures of these acids with water.

As regards the heats of hydration, the mixture of formic acid with gradually increasing quantities of water is at first an exothermic change, then endothermic, and finally exothermic; whilst that of acetic, propionic, and butyric acids is at first endothermic and then exothermic, but the heat evolution decreases after a certain degree of concentration. These results seem to indicate that the molecules of the three latter acids, in the liquid state, consist of complex molecules, the absorption of heat being conditioned by the dissociation.

V. H. V.

Products of the Dry Distillation of some Silver Salts of the Acetic Series. By F. Iwig and O. Hecht (*Ber.*, **19**, 238—242).—Chenevix stated (*Gilbert's Annalen*, **32**, 179) that when silver acetate is decomposed by heat, acetic acid free from acetone, carbonic

anhydride, and a hydrocarbon are evolved, the residue consisting of 95 per cent. silver and 5 per cent. carbon.

The authors have repeated Chenevix's experiments. The decomposition began when the thermometer in the bath employed showed 210°, went on freely at 240°, but required a higher temperature for completion. Pure acetic acid and carbonic anhydride were alone evolved, and the residue left in the retort consisted solely of a mixture of silver and carbon. 8·211 grams of silver acetate yielded 5·3049 grams of silver, 2·0940 grams of acetic acid, 0·5631 gram of carbonic anhydride, and 0·1284 gram of carbon (the loss not accounted for being 0·1206 gram). These results agree with the equation $4C_2H_3O_2Ag = 3C_2H_4O_2 + CO_2 + C + 4Ag$.

Similar experiments made with silver butyrate yielded butyric acid, carbonic anhydride, silver, and carbon, closely agreeing in quantities with those required by the equation $8C_4H_7O_2Ag = 7C_4H_8O_2 + CO_2 + 3C + 8Ag$. The decomposition was, however, not quite as regular as in the case of the acetate, the butyric acid not being quite pure, a little excess of carbonic anhydride being evolved, and the residue in the retort having a little resinous matter left with it. L. T. T.

Combination of Ethyl Acetate with Magnesium Chloride. By J. A. Le Canu (*Compt. rend.*, **102**, 363—365).—Anhydrous magnesium chloride dissolves in ethyl acetate much more readily than calcium chloride (Abstr., 1885, 371), and forms a viscous solution which deposits large quantities of crystals. It is very difficult to separate these crystals from the mother-liquor, but after being dried by means of kaolin their composition approximates closely to the formula $MgCl_2,2C_2H_3O_2Et$.

Strontium and barium chlorides are quite insoluble in ethyl acetate. Zinc chloride dissolves readily with great development of heat. The solution does not deposit crystals, but the ethyl acetate cannot be distilled off on the water-bath. Ferric chloride dissolves with a still greater development of heat and is partially reduced. C. H. B.

γ-Bromo- and γ-Iodo-butyric Acids. By L. Henry (*Compt. rend.*, **102**, 368—370).—γ-Bromo- and γ-iodo-butyric acids are readily obtained by the action of hydrobromic and hydriodic acids respectively on an aqueous solution of butyrolactone (this vol., p. 216).

γ-Iodobutyric acid, $CH_2I{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, crystallises in colourless lamellæ or tables, which become yellow when exposed to light, and melt at 40—41°. The corresponding iodopropionic acid melts at 82°. γ-Iodobutyric acid, unlike the β-derivative, is only slightly soluble even in warm water, but it dissolves readily in methyl alcohol, ether, carbon bisulphide, &c.

The alkyl salts are obtained by the action of sulphuric acid on a solution of the acid in methyl or ethyl alcohol. *Methyl γ-iodobutyrate* is a colourless liquid which boils at 198—200° without decomposition, has an agreeable odour, and is insoluble in water; sp. gr. at 5° = 1·666.

γ-Bromobutyric acid forms white, rhomboidal tables or lamellæ, which melt at 32—33°, and do not alter when exposed to air. It is

more soluble in water than the iodo-derivative, and dissolves readily in ether, carbon bisulphide, &c. Its alkyl salts are obtained by the action of sulphuric acid on its solution in the alcohols. They are colourless liquids which boil without decomposition, have an agreeable odour, and are insoluble in water. The methyl salt boils at 186—187° under a pressure of 757 mm.; sp. gr. at 5° = 1·450. The ethyl salt boils at 196—197° under a pressure of 748 mm.; sp. gr. at 5° = 1·363.

Comparison of the melting points of the derivatives of propionic and butyric acids shows that whereas the addition of CH_2 to propionic acid, converting it into butyric acid, raises the melting point about 20°, the addition of CH_2 to propionic derivatives, $CH_2X{\cdot}CH_2{\cdot}COOH$, converting them into butyric derivatives, $CH_2X{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, produces a considerable reduction in the melting point.

C. H. B.

Ethylpropylacetic Acid. By H. Kiliani (*Ber.*, **19**, 227—229).—*Ethylic ethylpropylacetoacetate* was obtained in the usual way from ethylic ethylacetoacetate, and at once saponified with strong alcoholic potash. *Ethylpropylacetic acid* thus obtained is a colourless oil, which boils at 209·2° (corr.) and does not solidify in a freezing mixture. The *calcium salt*, $(C_7H_{13}O_2)_2Ca + 2H_2O$, forms soft needles. 100 c.c. of water dissolve 11·4 grams of anhydrous salt at 19·5°. The *strontium salt* crystallises in small prisms with $2H_2O$. 100 c.c. of water dissolves 27·9 grams of anhydrous salt at 18·5°. The *silver*, *barium*, and *lead salts* all crystallise in colourless needles.

This acid is not the same as that obtained from the cyanhydrin of levulose (this vol., p. 438), but probably is the same as Hecht's isoheptylic acid, although there are discrepancies between the author's and Hecht's observations. Hecht intends to re-examine his acid.

L. T. T.

Coccerin from Living Cochineal. By C. Liebermann (*Ber.*, **19**, 328).—The author having obtained specimens of the living cochineal insect, is able to show that the peculiar waxy substance termed by him coccerin (Abstr., 1885, 1045) is really contained in the living animal, and is not produced during the preparation for commerce. The surface of the cactus on which the insects live was covered with what looked like white mould, but on further examination proved to be fragments of coccerin exuded by the insects. Several empty cocoons were examined and found to contain about three-fourths of their weight of coccerin.

A. J. G.

The Fat of Cochineal. By E. Raimann (*Monatsh. Chem.*, **6**, 891—898).—When dry cochineal is extracted with ether, and the solution washed with water, a brownish mass is obtained which soon deposits groups of needles. When the fat is saponified, the product washed with ether and acidified, myristic acid, or an isomeride, and two new acids of the acrylic series, $C_{14}H_{26}O_2$ and $C_{12}H_{22}O_2$, are obtained. The ethereal solution yielded two substances, probably alcoholic, $C_{36}H_{72}O$, melting at 66·6°, and $C_{15}H_{26}O$.

When cochineal, after being extracted with ether, is treated with

carbon bisulphide, a crystalline substance is obtained identical with Liebermann's coccerin (Abstr., 1885, 1045). N. H. M.

Action of Sulphuric on Oleic Acid. By A. Sabaneieff (*J. Russ. Chem. Soc.*, 1886, 35—49, and 87—98).—The author has investigated the product of the action of sulphuric acid on oleic acid, employed as a mordant under the name of "alizarin oil." The oleic acid used in the experiments was prepared from oil of sweet almonds, and thoroughly purified; it solidified at 6° to a white, crystalline mass, melting at 14°; in the liquid state, it was perfectly translucent and free from any taste or smell.

Oleic acid cooled down to at least 6°, when it becomes crystalline, was treated with sulphuric acid; the reaction under these conditions is not violent, and the temperature does not rise considerably, although the products of the reaction are the same as when oleic acid is used in the liquid state. An evolution of sulphurous anhydride is rarely observed. The reddish-brown product of the reaction, when treated with water, separates into two layers, of which one consists of aqueous sulphuric acid only; the other (which on neutralisation with alkali gives the so-called alzarin oil) was dissolved in ether, and subsequently treated with water, in which a portion only is soluble.

The portion insoluble in water consists partly of a solid substance, partly of a liquid; the former being more sparingly soluble in ether was freed from the latter by washing with this solvent. This solid substance evidently consists of a fatty acid; it melts after repeated crystallisation at 79°; the analytical data point to its being hydroxystearic acid, a view confirmed by determinations of the degree of saturation of the compound by means of Hübl's method (Abstr., 1884, 1435), the hydroxystearic acid was converted into iodostearic acid (identical with Saytzeff's compound, Abstr., 1885, 1049) and into stearic acid. The melting point of hydroxystearic acid, as determined by the author, differs somewhat from the data of former investigators (varying from 56° to 85·5°).

The liquid substance, after repeated washing with alcohol, gives a liquid residue which seems to be the anhydride of hydroxystearic acid; it is also obtained by heating the acid at 130—150°. It does not combine with bases, is sparingly soluble in alcohol, and is converted into the acid by boiling with alkalis; an attempt to convert the anhydride into the corresponding amide failed. The substance extracted by alcohol from the liquid portion contains in addition to a certain quantity of this anhydride and of hydroxystearic acid, an unsaturated liquid fatty acid, which seems to be unaltered oleic acid.

The portion of the product soluble in water was found to consist of sulphohydroxystearic acid, as proved by analysis of its copper salt, and by determination of its degree of saturation by Hubl's method. This sulphonic acid is easily decomposed, especially by heating it on the water-bath with hydrochloric acid, into hydroxystearic and sulphuric acids. Its aqueous solution always retains a certain amount of oleic and hydroxystearic acids and the anhydride of the latter.

On the whole, the experiments show that the duration of the reaction between oleic and sulphuric acid does not influence the quantity of sulphonic acid formed, 20 per cent. of the oleic acid being obtained as a rule in the form of this compound: 7·5—15 per cent. remain unchanged, and 70 per cent. is converted into hydroxystearic acid and its anhydride. These data, as well as the non-formation of sulphurous anhydride, do not agree with the explanations of this reaction proposed by former investigators (Müller-Jacobs, Liechti and Suida, Lukianoff); the author considers it most probable that the action of sulphuric acid on oleic acid consists of a series of simultaneous processes, partly yielding compounds of the two acids, not decomposed by water and dissolving therein, partly giving substances decomposed by water, which converts them into the insoluble substances described in the present paper. A. T.

Condensation of Members of the Carbamide-group with Ethyl Acetoacetate. By R. Behrend (*Ber.*, **19**, 219).—In continuation of his work on the condensation of carbamide with ethyl acetoacetate (Abstr., 1885, 246), the author has experimented with other members of the carbamide-group.

When phenyl carbamide is heated with ethyl acetoacetate and a little ether in closed tubes at 140—150°, it yields a yellow oil of the formula $C_{13}H_{16}N_2O_3$, which cannot be distilled. On saponification with alkalis, it yields acetone, alcohol, carbonic anhydride, and aniline; with acids, the same products are formed together with ethyl phenylcarbamate. L. T. T.

Action of Thiocarbamide on Ethyl Acetoacetate. By R. List (*Ber.*, **19**, 219—220).—By treating a mixture of ethyl acetoacetate and an alcoholic solution of thiocarbamide with a few drops of hydrochloric acid, an unstable ethereal salt is obtained, which on saponification yields the same compound, $C_5H_6N_2SO$, which Nencki and Sieber prepared by dissolving thiocarbamide in ethyl acetoacetate (Abstr., 1882, 501). The author considers this compound to be analogous to methyluranil and ascribes to it the formula

$$CS<\begin{matrix}NH\cdot CMe\\NH-CO\end{matrix}>CH.$$

L. T. T.

Action of Guanidine on Ethyl Acetoacetate. By A. Köhler (*Ber.*, **19**, 220—221).—By heating ethyl acetoacetate with an alcoholic solution of guanidine carbonate, a compound, $C_5H_7N_3O$, is obtained, which crystallises in prismatic needles, sparingly soluble in alcohol and cold water, more easily in boiling water. This substance has the properties both of an acid and of a base. Its formula is probably $NH:C<\begin{matrix}NH\cdot CMe\\NH—CO\end{matrix}>CH.$ L. T. T.

Influence of Ammonium Hydrogen Oxalate on the Solubility of the Normal Salt. By R. Engel (*Compt. rend.*, **102**, 365—368).—A solution of normal ammonium oxalate saturated at 0° contains

0·177 gram-molecule per litre, or 100 parts of water dissolve 2·215 grams of the salt; sp. gr. of the solution 1·0105.

The solubility of the acid oxalate cannot be accurately determined, because the salt partially dissociates in presence of water into the normal oxalate and the quadroxalate, part of the latter being precipitated. Equilibrium is only established after at least 48 hours. 100 grams of water at 0° dissolve at least 3·25 grams of acid ammonium oxalate, so that this salt is more soluble than the normal oxalate.

If successively increasing quantities of acid ammonium oxalate or oxalic acid, are added to a saturated solution of normal ammonium oxalate, as the quantity of free oxalic acid in the liquid increases in one geometric progression, the quantity of ammonium in solution in the form of normal or acid oxalate increases in another geometric progression. The curve is represented by the equation $m \log y = \log k + \log x$, in which y is the quantity of normal sulphuric acid, corresponding with the ammonia in 10 c.c. of the solution, x the quantity of normal potash solution required to neutralise the same quantity of liquid, and m and k are constants, with the values $m = 274$ and $\log k = 1{\cdot}517636$.

In four experiments the following numbers were obtained:—

Experiment.	Normal oxalate.	Acid oxalate.
1	3·54	0
2	2·65	1·45
3	2 475	2·525
4	2·38	2·9

The quantity of one oxalate diminishes as the other increases, and the addition of oxalic acid to a saturated solution of normal ammonium oxalate precipitates the normal oxalate and not oxalic acid.

If the saturated solution of both salts obtained in experiment 4 is mixed with small quantities of oxalic acid, and allowed to remain until equilibrium is established, it is found that neither the ammonium nor the acid in the liquid increases so long as it remains in contact with solid normal oxalate. This condition corresponds with the conversion of the normal oxalate into the acid salt. If on the other hand no solid normal salt is present, but the latter is wholly in solution, further additions of oxalic acid determine a sudden diminution in the proportion of ammonia, and the curve representing the phenomena is interrupted by a sudden fall which indicates the formation of a definite compound.

The above results indicate that when there is a great difference between the solubilities of the normal and acid salts, the less soluble should be almost insoluble in a saturated solution of the more soluble of the two. This is found to be the case with normal and acid potassium oxalates. C. H. B.

Formation of Ethyl Succinate. By O. Davidoff (*Ber.*, **19**, 406—408).—Diethyl succinate is produced by heating potassium succinate with ethylene bromide, and not ethylene succinate as

supposed by Richter. The formation of the ethyl succinate is confirmed by a vapour-density determination, and quantitatively by its decomposition with hydriodic acid.

The melting point of pure succinic acid is 185°, not 180°, as given in most text-books. V. H. V.

Ethyl Succinosuccinate. By A. Baeyer (*Ber.*, **19**, 428—433).—The author confirms the accuracy of Geuther's suggestion that the so-called ethyl quinonedihydrodicarboxylate, obtained by the action of bromine on ethyl succinosuccinate, is in reality ethyl paradihydroxyphthalate.

The compounds of ethyl succinosuccinate with phenylhydrazine have been described by Knorr. A hydroxylamine-derivative is obtained by the action of free hydroxylamine on ethyl succinosuccinate as a colourless crystalline mass, which was not further investigated. A *diimido-compound*, $C_{12}H_{18}N_2O_4$, is obtained by heating ethyl succinosuccinate with dry ammonium acetate. It crystallises in yellow needles, melts at 181°, is sparingly soluble in alcohol and ether, the solutions showing green fluorescence, more readily soluble in chloroform, and yields colourless salts with sulphuric and hydrochloric acids. Ethyl dihydroxyphthalate does not react with ammonia, phenylhydrazine, or hydroxylamine, even under most varied conditions; the difference in the behaviour of these two compounds is at once explicable on the assumption of the existence of hydroxyl-groups in the last-mentioned salt, and of ketone (CO) groups in the succinosuccinate.

Ethyl paradiamidoterephthalate, $C_6H_2(NH_2)_2(COOEt)_2$, is prepared by dissolving the above-described diimido-compound in sulphuric acid and gradually adding bromine (1 mol.) to the solution. It crystallises in lustrous, golden-yellow needles, melts at 168°, is sparingly soluble in alcohol and ether, to brown liquids showing a golden-yellow fluorescence; has strongly basic properties, and is readily saponified with alkalis. It is converted into terephthalic acid by first forming the diazo-compound, warming this with a solution of cuprous chloride in hydrochloric acid, and treating the chlorinated acid so formed with sodium amalgam in the cold.

When ethyl dihydroxyterephthalate is boiled with zinc and hydrochloric acid, it is readily reconverted into ethyl succinosuccinate.

It was incidentally noticed that terephthalic acid is converted into tetrahydroterephthalic acid by sodium amalgam at the temperature of the water-bath. A. J. G.

Sodium Potassium Racemates. By G. Wyrouboff (*Bull. Soc. Chim.*, **45**, 52—61).—Pasteur has stated that the conversion of racemates into lævo- and dextro-tartrates is due to the action of organic germs; this is, however, not correct, as perfectly stable racemates of the series $C_4H_4O_6NaM$ (M = Am, K, Rb) may be prepared, which are not altered on free exposure to the air; the true reason that racemates of this series cannot be crystallised from their solutions unaltered at the usual temperatures is, that at these temperatures the crystallised tartrates are less soluble than the racemates, and are consequently

deposited first; the curves of their solubilities are, however, not parallel in direction, and cut one another either above or below the normal temperatures, and at this point of section the solubilities alter in relation to one another, the tartrates becoming more soluble than the racemate, and the racemate may therefore be crystallised out unaltered from saturated solutions. The author has prepared sodium potassium racemate, $C_4H_4O_6NaK + 3H_2O$; at temperatures below 4°, it forms very fine colourless, monoclinic, rhombic crystals; it melts at 100°, and loses most of its water of crystallisation at 125°, and the remainder at 180°, at which temperature it begins to decompose; its sp. gr. = 1·783. By adding either a small crystal of the tartrate or the racemate to a saturated solution of this salt at a temperature of + 4° or + 5°, the point of intersection of the curves of the solubility of the two salts, either the racemate or the tartrate may be crystallised out at will, whilst at temperatures below this point only the racemate will crystallise out, and above it only the tartrates.

The sodium thallium racemate, $C_4H_4O_6NaTl + 2H_2O$, is never decomposed into the tartrates on crystallising from its aqueous solutions, and this is due to the very much greater solubility of the tartrates than the racemate; the difference between the two curves of solubility is so great that they do not intersect within the practical limits of temperature. Unsuccessful attempts were made to prepare sodium rubidium racemate. A. P.

Resolution of Optically Inactive Compounds. By E. Bichat (*Compt. rend.*, **102**, 428—431).—When saturated solutions of sodium or ammonium paratartrate, or the double salt, are allowed to cool in tubes protected from the air, crystals of the paratartrate are deposited, but if the solution cools in dishes with free exposure to air, crystals of the dextrotartrate and lævotartrate separate. This resolution of the paratartrate is not due to living organic matter in the air, for if solutions are sterilised and then inoculated with a small quantity of the mother-liquor in which resolution has taken place, all the usual precautions being observed, there is no development of organisms and the solution deposits the paratartrate. The separation of the dextro- and lævo-tartrates is therefore due to the introduction of inorganic particles from the air into the solutions, these inorganic particles being in all probability minute crystals of the dextro- and lævo-tartrates. C. H. B.

Bromopyromucic Acids. By H. B. Hill and C. R. Sanger (*Annalen*, **232**, 42—102).—*δ-Monobromopyromucic acid*,

$$CH\!\left<\begin{matrix}C(COOH)\\CH : CBr\end{matrix}\right>\!O,$$

is most conveniently prepared by the action of bromine-vapour at 100° on the acid. The properties of the substance have been previously described by the authors (Abstr., 1883, 912). The *barium* salt, $(C_5H_2BrO_3)_2Ba + 4H_2O$, crystallises in plates, and the *calcium* salt, $(C_5H_2BrO_3)_2Ca + 3H_2O$, in prisms. They are sparingly soluble in cold water. The *silver* salt forms small, crystalline plates, which are

sparingly soluble in boiling water. The *sodium* and *potassium* salts are anhydrous; the former crystallises in needles, the latter in plates.

Ethyl monobromopyromucate, prepared by the action of ethyl iodide on the silver salt, or by heating a mixture of the acid with alcohol and strong sulphuric acid, melts at 17° and boils at 235°. Its sp. gr. at 20° is 1·528. It is decomposed by strong ammonia at 100°, yielding the amide $C_5H_2BrO_2{\cdot}NH_2$. This compound crystallises in needles, melts at 144—145°, and dissolves freely in alcohol, ether, chloroform, and in hot water. The acid absorbs bromine vapour, forming δ-monobromopyromucic acid tetrabromide, $C_5H_3BrO_3Br_4$. This is soluble in ether, alcohol, or glacial acetic acid, but is decomposed by water. It decomposes at 173° without melting.

The action of bromine vapour on monobromopyromucic acid suspended in water, has been previously described (*loc. cit.*). On oxidation with nitric acid, δ-monobromopyromucic acid yields maleic and fumaric acids.

The preparation of *β-monobromopyromucic acid*,

$$CBr\begin{matrix}<\\ \\ \end{matrix}\begin{matrix}C(COOH)\\ -CH:CH-\end{matrix}\begin{matrix}\\ \\ >\end{matrix}O,$$

has been already described (Abstr., 1884, 1305). The acid melts at 128—129°, and the saturated aqueous solution at 18° contains 1·25 per cent. of the acid. The *barium* salt, $Ba(C_5H_2BrO_3)_2 + H_2O$, dissolves readily in hot water. The aqueous solution at 20° contains only 2·1 per cent. of the anhydrous salt. The *calcium* salt crystallises with 3 mols. H_2O in needles. The saturated solution at 20° contains 1·73 per cent. of $Ca(C_5H_2BrO_3)_2$. The crystalline *silver* salt is soluble in hot water. The *sodium* and *potassium* salts are anhydrous. *Ethyl β-monobromopyromucate* crystallises in prisms. It melts at 28—29°, and boils at 235°. The *amide*, $C_5H_2BrO_2{\cdot}NH_2$, forms silky needles, soluble in alcohol, ether, and in boiling chloroform. It melts at 155—156°.

β-Monobromopyromucic acid does not form an additive product with bromine, but on exposure to bromine vapour it is converted into β-δ-dibromopyromucic acid. The aqueous solution of the β-acid is readily attacked by bromine, yielding mucobromic acid, and on oxidation with dilute nitric acid it yields monobromofumaric acid.

The authors failed to obtain the third monobromopyromucic acid, melting at 156°, described by Schiff and Tassinari (Abstr., 1879, 308). Many of the properties of β-δ- and β-γ-dibromopyromucic acids, and the preparation of these acids by the action of an excess of alcoholic soda on pyromucic acid tetrabromide, have been previously described by Tönnies (Abstr., 1878, 785), and by the authors (Abstr., 1884, 1305). Small quantities of δ-monobromo- and tribromo-pyromucic acids, and di- and tri-bromofurfurane are also produced by this reaction. The β-δ-acid, $CBr\begin{matrix}<\\ \\ \end{matrix}\begin{matrix}C(COOH)\\ CH:CBr\end{matrix}\begin{matrix}\\ \\ >\end{matrix}O$, melts at 167—168°. A saturated aqueous solution of the *barium* salt, $Ba(C_5HBr_2O_3)_2 + 4H_2O$, contains 0·1 per cent. of the anhydrous salt at 16°. The *calcium* salt crystallises in prisms containing 3 mols. H_2O. At 17° the saturated solution contains 0·31 per cent. of the anhydrous salt. $C_5HBr_2O_3Ag$ is deposited

from hot water in prisms. The *potassium* and *sodium* salts crystallise in needles and are freely soluble in water; the former is anhydrous, the latter contains 2 mols. H_2O. *Ethyl-β-δ-dibromopyromucate*, $C_5HBr_2O_3Et$, melts at 57—58°, and boils at 271—272°. It crystallises in prisms which are soluble in ether, chloroform, benzene, and boiling alcohol. The *amide*, $C_5HBr_2O_2{\cdot}NH_2$, crystallises in silky needles. It melts at 175—176°, and dissolves freely in alcohol, ether, chloroform, and in boiling benzene. *β-δ-Dibromopyromucyl bromide*, $C_5HBr_2O_2Br$, obtained by the action of dry bromine on pyromucic acid, melts at 45—46°, and boils at 153—155° under 24 mm. pressure. It is soluble in alcohol, ether, chloroform, and benzene, and is converted into β-δ-dibromopyromucic acid by boiling in water.

β-γ-Dibromopyromucic acid, $CBr\begin{matrix}<\\ \\ \end{matrix}\begin{matrix}C(COOH)\\ CBr:CH\end{matrix}\begin{matrix}>\\ \\ \end{matrix}O$, melts at 191—192°. The following salts were prepared:—$Ba(C_5HBr_2O_3)_2 + 3H_2O$, forms flat needles; the saturated solution at 20° contains 0·36 per cent. of the anhydrous salt. $Ca(C_5HBr_2O_3)_2 + 5H_2O$ crystallises in needles; at 20° the saturated aqueous solution contains 1·16 per cent. of anhydrous salt. $AgC_5HBr_2O_3$ crystallises in needles. $C_5HBr_2O_3Na + 2H_2O$ forms silky needles, sparingly soluble in cold water. The anhydrous *potassium* salt, crystallising in prisms, is also sparingly soluble. The *ethylic* salt, $C_5HBr_2O_3Et$, melts at 67—68°, and dissolves freely in ether, chloroform, benzene, carbon bisulphide, light petroleum, and hot alcohol. The *amide*, $C_5HBr_2O_2{\cdot}NH_2$, melts at 195—196°, and dissolves readily in alcohol.

The aldehyde of dibromomaleic acid appears to be formed in small quantity by the action of bromine on β-γ-dibromopyromucic acid in the presence of water. This substance melts at 89—90°, and is soluble in alcohol, chloroform, ether, and benzene.

Tribromopyromucic acid, and the products of the action of bromine water and nitric acid on the acid, have already been described by the authors. An aqueous solution of the barium salt, $(C_5Br_3O_3)_2Ba + 3H_2O$, at 20° contains 0·2 per cent. of the anhydrous salt, and the aqueous solution of the calcium salt at the same temperature contains 0·55 per cent. $(C_5Br_3O_3)_2Ca + 4H_2O$ crystallises in needles. The sodium and potassium salts contain 1 mol. H_2O, and also crystallise in needles. Ethyl tribromopyromucate forms colourless prisms, soluble in ether, chloroform, benzene, and carbon bisulphide. It melts at 104°. The *amide*, $C_5Br_2O_2{\cdot}NH_2$, melts at 222—223°. It crystallises in needles which dissolve freely in warm alcohol. W. C. W.

Amides and their Nitro-derivatives. By A. P. N. Franchimont (*Rev. Trav. Chim.*, **4**, 195—212).—*Dinitrodimethyloxamide*,

$$NO_2{\cdot}NMe{\cdot}CO{\cdot}CO{\cdot}NMe{\cdot}NO_2,$$

obtained together with carbonic anhydride, nitrous oxide, and carbonic oxide, by dissolving dimethyloxamide in absolute nitric acid, crystallises in colourless needles which melt at 124°. Above its melting point, it decomposes rapidly into nitric acid, carbonic anhydride, and probably cyanogen and carbonic oxide. The formation of this dinitromethyloxamide is dependent upon the temperature.

Dinitrodimethylmalonamide, $CH_2(CO{\cdot}NMe{\cdot}NO_2)_2$, prepared in manner similar to the above compound, crystallises from alcohol in colourless prisms, which melt at 150°; it is readily soluble in ethyl acetate, sparingly soluble in chloroform, petroleum, and carbon bisulphide.

Dimethylisosuccinamide, from isosuccinyl chloride, or from the ethyl salt of methylmalonic acid, crystallises in small needles, which melt at 154°; it is readily soluble in water and alcohol, sparingly soluble in ether and benzene.

Tetramethylmalonamide, $CMe_2(CO{\cdot}NHMe)_2$, prepared from the methyl salt of dimethylmalonic acid, or from its chloride, crystallises in long needles, melts at 123°, and is very soluble in water and alcohol, sparingly soluble in ether.

Hexamethylmalonamide, $CMe_2(CO{\cdot}NMe_2)_2$, prepared from dimethylmalonyl chloride and dimethylamine, forms long prisms, melts at 80°, and distils apparently with partial decomposition at 276°. It is very soluble in water, alcohol, and ether. On treatment with nitric acid, dimethylmalonic acid is regenerated. At the conclusion of the paper, some remarks are offered on the action of nitric acid on different amides. V. H. V.

Formation of Furfurane and Thiophen from the Dioxide $C_7H_6O_2$. By S. Przibytek (*J. Russ. Chem. Soc.*, 1886, 123—124).—When the dioxide $C_4H_6O_2$, obtained by the action of potash on erythroldichlorhydrin (Abstr., 1884, 979), is heated for three days at 200—220° with anhydrous barium oxide, it is converted into furfurane; when heated with phosphorus pentasulphide at 170—180°, it yields thiophen. Both these reactions proceed slowly and in an incomplete manner, which is due, at least partly, to the formation of a solid polymeride of the dioxide. This amorphous, colourless substance, insoluble in water, is also formed by heating the dioxide at 170—180°, the transformation not being complete, and apparently limited by a maximum; above 200°, the polymeride is again slowly decomposed into the original compound. The investigation is continued.

A. T.

Croconic Acid and Leuconic Acid. By R. Nietzki and T. Benckiser (*Ber.*, **19**, 293—309; comp. Abstr., 1885, 779, 1127).—The material for this investigation was obtained by treating diamidotetrahydroxybenzene hydrochloride with potassium carbonate, manganic oxide, and water, and boiling for half an hour. To the filtrate, after acidifying with hydrochloric acid, barium chloride is added, when golden-yellow scales of barium croconate, $C_5O_5Ba + 3H_2O$ separate. The authors consider that the evidence is more in favour of the simple formula $C_5H_2O_5$ for croconic acid than the doubled formula $C_{10}H_4O_{10}$. They have failed to obtain the salt $C_{10}K_3HO_{10}$ described by Gmelin, although exactly following his directions; the brownish-yellow anhydrous needles obtained had the formula C_5KHO_5. A sodium potassium salt, C_5NaKO_5, was also obtained crystallising in sulphur-yellow rhombic tables. If the double formula is correct, three such double salts would be possible, but only the one could be obtained. The properties of croconic acid show clearly that it is a quinone.

Neither ethers nor acetyl-derivatives could be obtained. The anilides, of which several have been prepared and are under investigation, are red crystalline substances sparingly soluble in all solvents; as they have feebly acid properties, the hydroxyl groups are either not replaced, or at most only partly so.

When ammonium croconate is heated for some time with aqueous ammonia at 100°, a black powder of the formula $C_5H_3N_3O_2$ is obtained, which is insoluble in all solvents; it is probably a derivative of leuconic acid.

When croconic acid is reduced by stannous chloride, sulphurous acid, zinc-dust, &c., hydrocroconic acid is formed, and the liquid is decolorised; on heating, however, croconic acid is again formed, even in presence of a large excess of the reducing agent. Hydrocroconic acid could not be isolated, but the amount of sulphurous anhydride required for its production points to the formula $C_5H_4O_5$.

The substance obtained by Lerch by the action of hydriodic acid on croconic acid, and termed by him hydrocroconic acid, would seem to have a pinacone-like structure, and is termed by the authors croconic acid hydride. Its barium salt is best represented by the formula $C_{10}H_2O_{10}Ba_2 + 4H_2O$.

Thiocroconic acid is formed by the action of hydrogen sulphide on an acid solution of potassium croconate. The barium salt, $C_5SO_4Ba + 2H_2O$, crystallises in reddish-brown crystals of violet lustre. Lerch considered this substance to be a hydrothiocroconic acid.

Leuconic acid can be obtained in the crystalline state by adding finely powdered pure croconic acid to 6 to 8 parts of nitric acid of sp. gr. 1·36 cooled with ice; it then separates in small colourless needles. It has a sweet taste, is very soluble in water, sparingly in alcohol, nearly insoluble in ether, and can only be crystallised from nitric acid. Reducing agents convert it into croconic or hydrocroconic acids. The air-dried substance has the formula $C_5H_{10}O_{20}$; it loses half a mol. H_2O over sulphuric acid, and when dried at 100° has the formula $C_5H_8O_9$ ($=C_5O_5 + 4H_2O$). The substances formerly described as its salts are decomposition-products.

By the action of hydroxylamine on either leuconic or croconic acids, two substances are formed, of which one, $C_5N_5H_5O_5$, forms a voluminous, yellow precipitate, which by washing with water is changed into small globular aggregates of crystals; when heated to 172°, it decomposes with feeble explosion. It yields a potassium-derivative, $C_5H_3K_2O_5N_5$, which is obtained in brownish-yellow flocks and is highly explosive. There is little doubt that this substance is derived from leuconic acid by substitution of five hydroxylamine residues for five oxygen-atoms; it therefore has the constitution $C_5(NOH)_5$, whilst anhydrous leuconic acid must have the formula C_5O_5. The second hydroxylamine derivative resembles the first in appearance, but could not be obtained in a pure state.

In conclusion, the authors suggest the formula $<\begin{matrix}CO\cdot CO\\CO\cdot CO\end{matrix}>CO$ for anhydrous leuconic acid, but the free acid contains water, which is probably not in the form of water of crystallisation, but in similar union to that in chloral hydrate, the free acid being probably

$C_5(OH)_{10}$. Croconic acid may provisionally be expressed by the formula $<^{CO\cdot C(OH)}_{C(OH)\cdot CO}>CO$, but the position of the hydroxyl-groups has yet to be determined. A. J. G.

Influence of Light on the Action of Halogens on Aromatic Compounds. By J. Schramm (*Ber.*, **19**, 212—218).—Continuing his previous researches on this subject (Abstr., 1885, 518, 767, 888), the author has investigated the action of bromine on mesitylene and pseudocumene.

Mesitylene.—Bromine (1 mol.) acts energetically in the dark at ordinary temperatures, producing the monobromomesitylene, already obtained by Fittig and Storer, melting at −1°, and boiling at 226·5—227°, corr. (Fittig and Storer give 225°). This, when treated again with bromine in the dark, yields Süssenguth's dibromomesitylene melting at 64° (Abstr., 1883, 469), and finally tribromomesitylene. Thus, in the dark, the substitution takes place entirely in the benzene nucleus. Fittig and Hoogewerf (*Annalen*, **150**, 323) have observed the same effect with chlorine.

When bromine (1 mol.) is allowed to act on mesitylene in direct sunlight, a mixture of unaltered mesitylene and a *monobromomesityl bromide*, $C_6H_2BrMe_2\cdot CH_2Br$, is obtained. The latter compound cannot be distilled, and is still liquid at −19°. Treated with potassium acetate, it yields an acetate which partially decomposes when distilled. It was therefore at once saponified, and gave a *monobromomesityl alcohol*, $C_6H_2BrMe_2\cdot CH_2OH$ [= 4 : 3 : 5 : 1]. This substance crystallises in short broad needles, melts at 66—66·5°, and is soluble in alcohol, benzene, ether, chloroform, and light petroleum. It is easily oxidised to parabromomesitylic acid. When distilled, the alcohol is decomposed into water, monobromomesitaldehyde, and monobromomesitylene. Other decompositions take place simultaneously. When the above monobromomesityl bromide is treated in direct sunlight with bromine (1 mol.), another side group is attacked, a compound of the formula $C_6H_2BrMe(CH_2Br)_2$ being formed. It was obtained in too small quantity for the determination of its constitution, but is different from that obtained by Colson (Abstr., 1884, 57). It thus appears that mesitylene is indifferent to sunlight, bromination taking place in the nucleus both in the light and the dark, but that as soon as a monobromo-derivative has been formed the influence of light is felt, and substitution proceeds in the side groups. The author believes that this inactivity of sunlight is due to the meta-position of the side groups rendering the attack of the nucleus easy, a view supported by his observation that metaxylene is much more readily attacked in the dark than either ortho- or para-xylene.

Pseudocumene.—In the dark, bromination takes place entirely in the benzene nucleus, Beilstein and Kögler's monobromopseudocumene [Me : Me : Me : Br = 1 : 2 : 4 : 5], a *dibromopseudocumene*, crystallising in long, flat, and very pliant needles melting at 61·3°, and soluble in alcohol, benzene, and chloroform, and Fittig and Laubinger's tribromopseudocumene being formed.

In sunlight, the substitution readily takes place in the side groups.

Pseudocumyl bromide remains liquid at −17° and decomposes completely on distillation. When treated with bromine (1 mol.), a compound, $C_6H_3Me(CH_2Br)_2$ is formed, which crystallises in thin, silky needles, melting at 97—97·5°, and is soluble in benzene, toluene, alcohol, and petroleum. L. T. T.

Dichlorotoluenes and Dichlorobenzoic Acids. By E. Lellmann and C. Klotz (*Annalen*, **231**, 308—326).—*Unsymmetrical Orthodichlorotoluene*, $C_6H_3MeCl_2$ [1 : 3 : 4], *and Dichlorobenzoic Acid.*—In order to prepare metachloroparacetotoluide, chlorine is passed into a solution of paracetotoluide in glacial acetic acid until the mixture begins to crystallise. The flask in which the operation takes place must be surrounded by ice-cold water. The crystalline mass is rapidly filtered by means of a filter-pump, and the crude product may be purified by recrystallisation from alcohol. The pure metachloroparacetotoluide melts at 114—115°, not at 99° as stated by Wroblevski (this Journal, 1874, 54). The crude product is converted into metachloroparatoluidine by boiling with hydrochloric acid. The free base is liberated from the hydrochloride by an alkali, and is purified by distillation in a current of steam. It melts at 7°, and boils at 218—219° under 732 mm. pressure. The hydrochloride is converted into dichlorotoluene by Sandmeyer's process (Abstr., 1884, 1311; and 1885, 149). The pure product boils at 200·5° under 741 mm. pressure. Its sp. gr. is 1·2512 at 20° compared with water at the same temperature. It is easily oxidised to orthodichlorobenzoic acid (m.p. 201°) by the action of nitric acid (4 vols. concentrated acid to 9 of water) in sealed tubes at 130°.

Unsymmetrical metadichlorotoluene, $C_6H_3MeCl_2$ [= 1 : 2 : 4], is obtained from orthochloroparatoluidine hydrochloride by a process similar to the above (the chlorotoluidine is prepared by reducing orthochloroparanitrotoluene with tin and hydrochloric acid). The dichlorotoluene is a colourless refractive liquid of sp. gr. 1·24597 at 20°. It boils at 194° under a pressure of 745 mm. It is less easily oxidised by nitric acid than the orthodichlorotoluene. *Metadichlorobenzoic acid* melts at 158°. It forms long needles which are freely soluble in alcohol. The *barium* salt, $Ba(C_7H_3Cl_2O_2)_2 + 3\frac{1}{2}\ H_2O$, crystallises in needles.

Paradichlorotoluene, $C_6H_3MeCl_2$ [1 : 2 : 5], is obtained from orthacetotoluide by the same process as that employed for preparing orthodichlorotoluene from paracetotoluide. Chlororthacetotoluide melts at 140°. It is decomposed by boiling with strong hydrochloric acid, yielding *metachlororthotoluidine hydrochloride*, which crystallises in red plates, soluble in alcohol and in hot water. The free base melts at 29—30°, and boils at 236—238° under 730 mm. pressure. *Paradichlorotoluene* is a refractive liquid, which solidifies at 4°, and boils at 194° under 745 mm. pressure. On oxidation with nitric acid, it yields *paradichlorobenzoic acid*, melting at 153·5°. The barium salt crystallises in needles, containing $3\frac{1}{2}$ mols. H_2O. This acid seems to be identical with that which Beilstein (this Journal, 1876, i, 587) obtained by the action of chlorine on orthochlorobenzoic acid, and Clans (this Journal, 1877, ii, 782) obtained by the chlorina-

tion of benzoic acid. It is perhaps identical with the acid melting at 156° which Schultz prepared from dichlorobenzotrichloride.

Symmetrical Metadichlorotoluene, $C_6H_3MeCl_2$ [= 1 : 3 : 5].—*Metachloroparacetotoluide*, prepared from metachloroparatoluidine, melts at 115°. On chlorination, it yields unsymmetrical *metadichloroparacetotoluide*, which is deposited from alcohol or ether in long needle-shaped crystals. It is insoluble in water and melts at 201°. It is converted into unsymmetrical *metadichloroparatoluidine*,

$$C_6H_2MeCl_2{\cdot}NH_2\ [Me : Cl : NH_2 : Cl = 1 : 3 : 4 : 5],$$

by the action of strong hydrochloric acid at 120°. This substance is freely soluble in alcohol and ether. It crystallises in needles melting at 60°. It does not combine with hydrochloric acid. Symmetrical metadichlorotoluene is prepared by the action of ethyl nitrite on a solution of the base in strong sulphuric acid.

Dichlorotoluene melts at 26°, and boils at 195° under 729 mm. pressure. It yields symmetrical *metadichlorobenzoic acid* on oxidation. This acid dissolves freely in alcohol and melts at 182—182·5°. At a higher temperature, it sublimes in long, flexible needles. The barium salt crystallises in white plates.

The dichlorobenzoic acid melting at 126·5°, described by Schultz, appears to be a mixture of two isomerides. W. C. W.

The Propyl-group in the Cumyl and Cymene Series. By O. Widman (*Ber.*, **19**, 251—255).—From a consideration of all the known intermolecular changes of the propyl-group into the isopropyl-group, or *vice versâ*, in these series, the author deduces the rule that where a methyl-group occupies the para-position relatively to a propyl-group, it exerts a predisposing influence towards the formation of normal propyl; on the other hand, with a carboxyl-group in the same position, the influence tends to the formation of isopropyl.

A. J. G.

Nitrosophenol Hypochlorite. By R. Möhlau (*Ber.*, **19**, 280—283).—This compound is prepared by dissolving 1 gram of nitrosophenol in 500 c.c. of water, adding 5 c.c. of hydrochloric acid, and then running in a solution of bleaching powder until a distinct odour of hypochlorous acid is observed. It crystallises in slender, yellow needles of the formula $C_6H_4NO_2Cl$, explodes when quickly heated to about 70°, or when touched with a drop of strong sulphuric or nitric acid, and gives Liebermann's reaction. It reacts energetically with amines and phenols, is resolved into nitrosophenol and hypochlorous acid by alkalis, and when heated with dilute sulphuric acid is decomposed into quinone, hydroxylamine, and hypochlorous acid. Acetophenonoxime also unites with hypochlorous acid. A. J. G.

New Picrates. By A. Smolka (*Monatsh. Chem.*, **6**, 915—926).—*Ethylamine picrate* forms yellow crystals, melts at 165°, and is soluble in alcohol. *Asparagine picrate*, $C_4H_8N_2O_3,C_6H_3N_3O_7$, crystallises in yellow, lustrous prisms, sparingly soluble in alcohol. When heated at 180°, it decomposes without melting. *Urea picrate*,

$CO(NH_2)_2,C_6H_3N_3O_7$, crystallises in slender, yellow needles, having a silky lustre, readily soluble in alcohol, sparingly in water; it melts at 142° with decomposition. Aniline picrate forms transparent crystals, yellow by transmitted, and brownish-yellow by reflected light. It is decomposed by boiling water; when heated to 165° it blackens. *Para-toluidine picrate* crystallises from alcohol, in which it is readily soluble, in long flat prisms; it melts at 169° with decomposition. *α-Naphthyl-amine picrate* forms groups of greenish-yellow, very lustrous prisms, soluble in alcohol, sparingly soluble in water. Prolonged boiling with water decomposes it slightly. It melts with decomposition at 161°. N. H. M.

Derivatives of Methyl Ethyl Quinol. By F. Fiala (*Monatsh. Chem.*, **6**, 912—914).—*Methyl ethyl tetrachloro-quinol*, $OMe\cdot C_6Cl_4\cdot OEt$, is obtained by saturating a well-cooled solution of methyl ethyl quinol in glacial acetic acid with chlorine, and keeping the product in a vacuum over lime; the whole solidifies to a mass of matted, yellowish-white needles. It crystallises from alcohol in colourless, lustrous needles melting at 101° (uncorr.); when heated above its melting point, it sublimes in long, hair-like crystals. It is very electric. It dissolves readily in benzene, light petroleum, and ether, sparingly in alcohol and glacial acetic acid.

Methyl ethyl dibromo-quinol, $OMe\cdot C_6H_2Br_2\cdot OEt$, is obtained by the action of bromine on methyl ethyl quinol dissolved in glacial acetic acid. The product is treated with a small quantity of water and placed in a vacuum over sulphuric acid; the crystals which separate are pressed in a calico filter and crystallised from glacial acetic acid and alcohol. It forms colourless crystals with a fatty lustre, melting at 88°, and is readily soluble in ether, glacial acetic acid, benzene, &c., sparingly in alcohol.

Methyl ethyl dinitro-quinol, $OMe\cdot C_6H_2(NO_2)_2\cdot OEt$, is prepared by treating a cooled solution of the ether in glacial acetic acid with an equal volume of nitric acid. It crystallises in sulphur-coloured needles, melting at 144° (uncorr.). When exposed to air, it becomes red. It dissolves readily in glacial acetic acid and in alcohol, more sparingly in ether, benzene, and light petroleum. N. H. M.

Mixed Ethers of Quinol. By F. Fiala (*Monatsh. Chem.*, **6**, 909—911; compare Abstr., 1884, 1138).—*Methyl isoamyl quinol*, $OMe\cdot C_6H_4\cdot OC_5H_{11}$, is a clear oil, boiling at 234—237° (uncorr.). *Ethyl propyl quinol*, $OEt\cdot C_6H_4\cdot OPr$, crystallises from glacial acetic acid in lustrous, colourless plates which melt at 36° (uncorr.). *Ethyl isobutyl quinol*, $OEt\cdot C_6H_4\cdot OC_4H_9$, forms colourless plates, melting at 39° (uncorr.). *Ethyl isoamyl quinol*, $OEt\cdot C_6H_4\cdot OC_5H_{11}$, is a colourless, oily substance, boiling at 251—252° with partial decomposition. When kept long, it becomes reddish-brown. *Propyl isobutyl quinol*, $OPr\cdot C_6H_4\cdot OC_4H_9$, forms a colourless oil, which becomes brown when kept; it boils at 244—245° (uncorr.).

These compounds are prepared as already described (*loc. cit.*) at a temperature not above 150°; the yield is then 40—50 per cent. of the theoretical. They all dissolve readily in benzene, light petroleum,

chloroform, &c., and have an agreeable, aromatic odour. They reduce ammoniacal silver solution at the ordinary temperature.

N. H. M.

Oxidation of Phthalic Alcohol. By E. Hjelt (*Ber.*, **19**, 411—412).—By the oxidation of phthalic alcohol with chromic mixture, a thick, viscid oil is obtained containing phthalaldehyde, phthalide, and unaltered phthalic alcohol. All attempts to isolate phthalaldehyde from this mixture were fruitless. The aldehyde is sparingly soluble in water, volatilises with difficulty in steam, and reduces ammoniacal silver solutions; under certain conditions, it is readily converted into its isomeride, phthalide. The preparation of the aldehyde was attempted by several other methods, but in all cases without success.

A. J. G.

Reaction of Primary and Secondary Amines. By P. v. Romburgh (*Rec. Trav. Chim.*, **4**, 189—195).—Di- and tri-nitro-halogen-derivatives of benzene react with primary and secondary amines to form crystalline products derived from the benzene-compound by the replacement of the halogen by the residue of the amine. The compounds thus obtained yield nitramines when treated with fuming nitric acid.

Thus, with dinitrobromobenzene, propylamine forms *dinitrophenylpropylamine*, $C_6H_3(NO_2)_2{\cdot}NHPr$, crystallising in yellow needles which melt at 95°; with trinitrochlorobenzene, ($NO_2 : NO_2 : NO_2 : Cl = 1 : 2 : 4 : 6$), a *trinitrophenylpropylamine*, $C_6H_2(NO_2)_3{\cdot}NHPr$, in yellow needles, melting at 59°. Both these substances on treatment with fuming nitric acid form *trinitrophenylpropylnitramine*,

$$C_6H_2(NO_2)_3NPr{\cdot}NO_2,$$

crystallising in yellow plates which melt at 97°. Such reactions are characteristic of the primary and secondary amines, and in the following table the melting points of such crystalline derivatives are given:—

Amines.	Dinitrophenyl-derivatives.	Trinitrophenyl-derivatives.	Nitramines.
Methylamine ..	178°	111—112°	127°
Dimethylamine .	87	138	
Ethylamine	113	84	96
Diethylamine...	80	164	
Allylamine.....	75—76	80	?
Isobutylamime..	80	95	110

V. H. V.

Action of Paratoluidine on Resorcinol and Quinol. By A. Hatschek and A. Zega (*J. pr. Chem.* [2], **33**, 209—241).—*Metahydroxyphenylparatolylamine*, $OH{\cdot}C_6H_4{\cdot}NH{\cdot}C_7H_7$, is obtained by heating resorcinol with paratoluidine and anhydrous calcium chloride, in the proportions 1 : 2 : 2, for eight hours at 200°. The oily product so obtained solidifies after some time to a crystalline mass, and is distilled. The fraction boiling at 330—370° is decolorised by distilling in superheated steam or by repeated distillation in hydrogen. It crys-

tallises from benzene and light petroleum (mixed) in small, lustrous needles melting at 91° and boils at 350°. It is readily soluble in alcohol, ether, and benzene, &c.; sparingly soluble in light petroleum and boiling water. The *sodium salt* forms groups of long, white needles which soon decompose when exposed to air. The *hydrochloride*, $C_{13}H_{13}NO,HCl$, is very unstable; it is completely decomposed by water.

Formylmetahydroxyphenylparatolylamine, $OH\cdot C_6H_4\cdot N(C_7H_7)\cdot CHO$, is obtained by warming the base with an excess of formic acid in a reflux apparatus for two hours; it dissolves readily in ether, acetone, &c., and melts at 146°. The *dibenzoyl-derivative*, $BzO\cdot C_6H_4\cdot NBz\cdot C_7H_7$, is formed when the base is heated with benzoyl chloride for ½ to 1 hour at 120—130°. It melts at about 105°. When dissolved in fuming nitric acid, and the solution after 12 hours poured into water, *dibenzoyldinitrometahydroxyphenylparatolylamine*, $C_{27}H_{19}(NO_2)_2O_3$, is formed. This crystallises from alcohol in slender, yellow needles and melts at 110°.

Nitrosometahydroxyphenylparatolylamine, $OH\cdot C_6H_4\cdot N(NO)\cdot C_7H_7$, is prepared by treating an alcoholic solution of the hydroxy-base with the theoretical amount of sodium nitrite dissolved in a little water, and then adding hydrochloric acid. The intense reddish-brown solution thus obtained gradually deposits thick, black prisms, which crystallise from dilute alcohol in long, yellow needles melting at 105°, and are readily soluble in hot alcohol, ether, benzene, &c. *Ethyl ethoxyphenylparatolylamine*, $OEt\cdot C_6H_4\cdot NEt\cdot C_7H_7$, is obtained by the action of ethyl iodide and potash on the hydroxy-base; it is an orange-coloured liquid, which gradually becomes dark-coloured.

When metahydroxyphenylparatolylamine is distilled with zinc-dust, it yields phenylparatolylamine.

Diparatolylmetaphenylenediamine, $C_6H_4(NH\cdot C_7H_7)_2$, is formed in the preparation of hydroxyphenylparatolylamine, but is best obtained by heating 1 part of resorcinol with 4 parts of paratoluidine and 2 parts of a mixture of calcium and zinc chlorides (1 : 5) for 20 to 24 hours at 240°. It forms groups of white, lustrous needles, melts at 137°, and is readily soluble in hot alcohol, ether, benzene, and glacial acetic acid. It distils with decomposition at a high temperature. The *hydrochloride* forms a white, crystalline powder and is readily decomposed by water. The *diacetyl-derivative*, $C_6H_4(NAc\cdot C_7H_7)_2$, forms small lustrous grains, readily soluble in warm benzene and alcohol; it melts at 176°. The *dibenzoyl-compound*, $C_6H_4(NBz\cdot C_7H_7)_2$, crystallises from alcohol in pale yellow, short needles melting at 152°; it dissolves readily in benzene, sparingly in ether.

Dinitrosodiparatolylmetaphenylenediamine, $C_6H_4[N(NO)C_7H_7]_2$, is obtained by adding powdered sodium nitrite to a solution of the diamine in benzene in presence of glacial acetic acid and shaking well. It crystallises from a mixture of benzene and alcohol in slender, yellow needles which decompose when heated to 150°. It is readily soluble in warm alcohol and benzene.

Dimethyldiparatolylmetaphenylenediamine, $C_6H_4(NMe\cdot C_7H_7)_2$, is obtained by heating the diamine (1 mol.) with methyl iodide and potash (each 2 mols.) at 150°. It forms a reddish-brown oil

boiling at 400°; when exposed to air, it becomes dark and acquires a green fluorescence. It has the odour of geranium.

Parahydroxyphenylparatolylamine, $OH\cdot C_6H_4\cdot NH\cdot C_7H_7$, is formed when quinol is heated with twice its weight of paratoluidine and calcium chloride for eight hours at 260°. The solid product is then warmed and the portion thus liquefied poured from the solid calcium chloride; it is then distilled, and the fraction boiling at 330—370° redistilled in a current of hydrogen. It crystallises in white plates melting at 122°; is readily soluble in benzene, alcohol, and hot glacial acetic acid, and boils at 350—360°. It yields readily soluble unstable compounds with alkalis. The *hydrochloride* forms white flakes which are completely decomposed by water. The *diacetyl*-derivative, $OAc\cdot C_6H_4\cdot NAcC_7H_7$ forms large, transparent plates readily soluble in warm alcohol; it melts at 101°. The *dibenzoyl-compound*,

$$OBz\cdot C_6H_4\cdot NBzC_7H_7,$$

crystallises in small, short, colourless prisms melting at 169°, and readily soluble in boiling alcohol and warm benzene. *Nitrosoparahydroxyphenylparatolylamine*, $OH\cdot C_6H_4\cdot N(NO)C_7H_7$, melts with decomposition at 130°; it could not be obtained in the pure state.

Ethylparethoxyphenylparatolylamine, $OEt\cdot C_6H_4\cdot NEtC_7H_7$, is prepared in a manner similar to the ethylmetethoxy-compound, and is purified by distilling in hydrogen. It forms bright yellowish-brown globular aggregates, readily soluble in alcohol, ether, and benzene; it boils at 340°. The *methyl-derivative* boils at 330°; it does not solidify completely.

When parahydroxyphenylparatolylamine is distilled with zinc-dust it yields phenylparatolylamine.

Diparatolylparaphenylenediamine, $C_6H_4(NH\cdot C_7H_7)_2$, is prepared similarly to diparatolylmetaphenylenediamine, and forms very lustrous plates melting at 182°. It is sparingly soluble in boiling alcohol, rather more so in boiling benzene and glacial acetic acid. It dissolves in sulphuric acid, forming a colourless solution, but a trace of nitric acid or of a nitrite causes a splendid deep blue coloration, very characteristic of the para-compound. The *hydrochloride* forms a white crystalline unstable compound. The *diacetyl-derivative*,

$$C_6H_4(NAc\cdot C_7H_7)_2,$$

crystallises in yellowish rhombohedra melting at 172—173°, readily soluble in boiling glacial acetic acid, alcohol, and benzene. The *dibenzoyl-derivative*, $C_6H_4(NBzC_7H_7)_2$, forms small, slightly brown scales which melt at 222°; it dissolves readily in hot alcohol and benzene. The *dinitroso-derivative*, $C_6H_4[N(NO)C_7H_7]_2$, crystallises in lemon-coloured plates, soluble in alcohol and benzene; it melts at 152°. *Dimethyldiparatolylparaphenylenediamine*, $C_6H_4(NMeC_7H_7)_2$, is prepared in a manner similar to its isomeride obtained from diparatolylmetaphenylenediamine, and forms colourless needles melting at 153°.

Aniline and orthotoluidine react with parahydroxyphenylparatolylamine in presence of zinc or calcium chloride, with formation, on the one hand, of diphenyl- and diparatolyl-paraphenylenediamine, and on the other, of dipara- and diortho-tolylparaphenylenediamine.

N. H. M.

Condensation of Chloral Hydrate with Tertiary Amines. By P. Boessneck (*Ber.*, **19**, 365—369).—The former observations on the production of dimethamidobenzaldehyde (Abstr., 1885, 976) by heating dimethylaniline with chloral hydrate in presence of zinc chloride are confirmed. This substance when treated with a further quantity of dimethylaniline in presence of zinc chloride, or preferably by passing in dry hydrogen chloride, at a temperature of 170°, yields hexamethylparaleucaniline.

Diethylaniline when treated with chloral hydrate and zinc chloride at a temperature of 100°, yields a substance of the composition $C_2H(C_6H_4\cdot NEt_2)_5$. This is a white solid mass melting at 158°, and yielding a bluish-green dye when oxidised. If the reaction is effected at a temperature of 40°, *diethamidohydroxyphenyltrichlorethane hydrochloride*, $NEt_2\cdot C_6H_4\cdot CH(OH)\cdot CCl_3,HCl$, is produced, which crystallises in cubes and is decomposed by alkalis to form *paradiethamidobenzaldehyde*, $NEt_2\cdot C_6H_4\cdot CHO$, which crystallises in needles melting at 41°, and is soluble in the ordinary menstrua. V. H. V.

Compounds of Perchloromethylmercaptan with Aromatic Amines. By B. Rathke (*Ber.*, **19**, 395—396).—In an examination of the properties of perchloromethylmercaptan, the author has shown that it reacts with aniline thus: $CCl_3SCl + NH_2Ph : CCl_3\cdot S\cdot NHPh + HCl$; on adding alcoholic potash or ammonia to a concentrated ethereal solution of the product, prismatic crystals separate to which the formula $CHCl_2\cdot SOPh$ was formerly ascribed. It is now found that this compound contains nitrogen, and the analytical results given point to a composition $C_7H_5NSCl_3$. The compound assumes a red colour at 136°, and melts at 140°; when quickly heated, it evolves red fumes, probably of azobenzene, with slight explosion. To it is ascribed the constitution $S<\begin{matrix}CCl_2\\NPh\end{matrix}>$, or more probably $S<\begin{matrix}CCl_2\cdot NPh\\NPh\cdot CCl_2\end{matrix}>S$.

Paratoluidine forms a similar compound crystallising in white needles which melt at 138°; it is far more stable than the aniline-derivative. The compound from orthotoluidine is crystalline, and melts about 134° with incipient carbonisation, and evolution of gas. V. H. V.

Azocumene. By V. Pospekhoff (*J. Russ. Chem. Soc.*, 1886, 49—55).—Isopropylbenzene was obtained by the action of isopropyl bromide on benzene in the presence of aluminium bromide (Gustavson, Abstr., 1878, 972). This synthetical cumene, boiling at 151—153°, was converted into *nitrocumene*, a slightly yellowish liquid, rapidly becoming yellow under the influence of air and light; at 165—170°, it grows more and more viscous, its colour darkens, and at higher temperatures it apparently decomposes entirely. In a mixture of solid carbonic anhydride and ether, it solidifies to a wax-like mass, which melts at — 35°. This nitrocumene was reduced in alcoholic solution with sodium amalgam, and on pouring the product of the reaction into water, a dark-red almost brown mass is obtained, consisting of solid azocumene and a certain quantity of a red oil, not

yet investigated; the quantity of this oil is diminished by using dilute solutions of nitrocumene.

Azocumene, after repeated recrystallisation from alcohol, is obtained in the form of thin leaflets of light yellow colour, melting at 107·5°, easily soluble in ether, benzene, and hot alcohol, sparingly in cold alcohol. 100 parts of alcohol (sp. gr. 0·796 at 17°) at 19° dissolve 1·7486 parts, and at 19·2°, 2·0456 parts of azocumene; 100 parts of ether at 16·4° dissolve 28·9932, and at 15·2°, 19·6612 parts of azocumene. Azocumene, like azobenzene and unsymmetrical azotoluene, absorbs benzene vapour, forming a red liquid which, on exposure to air, gives off benzene and leaves an amorphous mass of the azo-compound.

By reducing nitrocumene in alcoholic alkaline solution with excess of zinc-dust, *hydrazocumene* is formed; this compound, when subjected to crystallisation from alcohol or benzene, was entirely oxidised to azocumene. A. T.

Diazo-compounds. By P. Griess (*Ber.*, **19**, 313—320).—When triazobenzene, N_3Ph (diazobenzenimide azophenylenediamine), is heated with strong hydrochloric acid, it is completely converted into a mixture of ortho- and para-chloraniline, and when heated with moderately concentrated sulphuric acid (1 : 1) it yields paramidophenol.

Triazobenzoic acid, $N_3{\cdot}C_6H_4{\cdot}COOH$ (metadiazobenzoic acid imide), when boiled with hydrochloric acid yields parachlorometamidobenzoic acid and a new isomeride thereof. This acid [$COOH : Cl : NH_2 = 1 : 2 : 3$] crystallises in white tables or small prisms, melts at 185°, is readily soluble in alcohol and ether, and has strongly marked acid properties.

In a previous paper (Abstr., 1884, 1148), the author has stated that diamido-compounds in which the amido-groups are in the meta-position relatively to one another, are not converted into diazo-compounds by the action of nitrous acid, but into substances of the triamidoazobenzene type. He now finds, however, that diazo-compounds are formed if a very large excess of nitrous acid is used in presence of much free hydrochloric acid.

Metabidiazobenzene Compounds.—The chloride could not be obtained in the solid form owing to its instability; the *platinochloride*, $C_6H_4(N_2Cl)_2,PtCl_4$, crystallises in very small, roundish, yellow plates, nearly insoluble in cold water and alcohol, but decomposed with evolution of nitrogen when heated with these liquids. The dry salt explodes violently when heated. The *aurochloride*,

$$C_6H_4(N_2Cl)_2,2AuCl_3,$$

is obtained as an explosive precipitate consisting of microscopic, yellow needles. These salts resemble those of other diazo-compounds in their reactions: thus they yield metadichlorobenzene when heated with soda. When the platinochloride is treated with an aqueous solution of phenylenediamine hydrochloride, a blackish-brown, scarcely crystalline substance, probably of the formula $C_6H_4(N_2{\cdot}C_6H_4{\cdot}NH_2)_2$, is obtained, whilst with β-naphtholdisulphonic acid it yields a readily soluble yellowish-red dye of the formula $C_6H_4[N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH]_2$.

Similar bidiazo-compounds have been prepared from other meta-compounds, such as metadiamidotoluene, and metadiamidonitrophenol, of which only the platinochloride of the last-named substance,

$$\left[<^{O}_{N_2}>C_6H_2(NO_2)\cdot N_2Cl\right]_2,PtCl_4,$$

is described; it crystallises in well-formed, six-sided, yellow tables or prisms.

Paraphenylenediamine is completely converted into the bidiazo-compound if diazotised under the conditions above-mentioned. The platinochloride, $C_6H_4(N_2Cl)_2,PtCl_4$, is obtained as a yellow, crystalline, explosive precipitate. A. J. G.

Preparation of Methyl-violet. By B. Rathke (*Ber.*, **19**, 397—400).—In this paper, the patented process for the preparation of methyl-violet from dimethylaniline and perchloromethylmercaptan is more minutely examined. On boiling the crude product with water, tarry masses separate which can be redissolved in acid; the liquid on evaporation or addition of a solution of salt yields crystals of *hexamethylparaleucaniline*. In the mother-liquor from this substance, as also in the tar, the subsidiary products *dimethylaniline sulphide* and *leuco-violet* are present. The author explains the reactions which lead to the formation of these substances as follows: the perchloromethyl-mercaptan is decomposed into carbon tetrachloride and sulphur, of which the former reacts with dimethylaniline to form methyl-violet thus: $CCl_4 + 3NMe_2Ph = 3HCl + C(C_6H_4\cdot NMe_2)_3Cl$, whilst the latter yields dimethylaniline sulphide, $S + 2NMe_2\cdot C_6H_5 = S(C_6H_4\cdot NMe_2)_2 + H_2$, the hydrogen serving to reduce the methyl-violet in part to the leuco-derivative. V. H. V.

Reduction Products of Aromatic Aldehydes. By F. Tiemann (*Ber.*, **19**, 354—359).—When benzaldehyde is heated with zinc-dust and acetic acid for twelve hours in a reflux apparatus, benzyl acetate is formed. With parahydroxybenzaldehyde, the reaction proceeds rather differently, *dipara-acetoxyisohydrobenzoin*,

$$OAc\cdot C_6H_4\cdot \overset{1}{C}H(OH)\cdot \overset{1}{C}H(OH)\cdot C_6H_4\cdot OAc,$$

being formed; this crystallises in small white needles, melts at 192°, cannot be distilled unchanged, is sparingly soluble in water, readily in alcohol, ether, benzene, and chloroform, and is insoluble in alkalis in the cold. *Diparahydroxyisohydrobenzoin*,

$$OH\cdot C_6H_4\cdot CH(OH)\cdot CH(OH)\cdot C_6H_4\cdot OH,$$

is obtained from the acetoxy-compound by heating it with aqueous potash and alcohol. It melts at 197—198°, and is identical with the substance obtained by Herzfeld as one of the products of the action of sodium amalgam on parahydroxybenzaldehyde, and erroneously considered by him to be parahydroxybenzyl alcohol (Abstr., 1878, 65).

When salicylaldehyde is treated in similar manner, a substance of the formula $C_{14}H_{10}O_2$, is obtained; it crystallises in slender, white

needles, melts at 82°, boils without decomposition at 215—220° under 30—40 mm. pressure, and is sparingly soluble in water, readily in alcohol, ether, chloroform, and light petroleum. It must be regarded as the inner anhydride of diorthohydroxyhydrobenzoin.

Parahydroxybenzyl alcohol seems to be formed by the action of sodium on an alcoholic solution of parahydroxybenzaldehyde; it is being examined. A. J. G.

Terephthaldehyde. By W. Löw (*Annalen*, **231**, 361—384).—Terephthaldehyde and the products of its oxidation and nitration have been previously described by the author (Abstr., 1885, 799). A concentrated solution of sodium hydroxide decomposes terephthaldehyde, forming paraxylylene alcohol, and parahydroxybenzoic and terephthalic acids. On the addition of ammonia to an alcoholic solution of terephthaldehyde, the hydrobenzamide is deposited as a white precipitate, insoluble in alcohol and ether. It is decomposed by boiling with water or dilute acids into ammonia and terephthaldehyde.

Paraldehydocinnamic acid, $COH \cdot C_6H_4 \cdot C_2H_2 \cdot COOH$, is formed by the action of sodium acetate and acetic anhydride on terephthaldehyde at 160°. It crystallises in prisms, soluble in hot acetic acid. It melts at 247°, and sublimes in large plates. The acid reduces silver salts with difficulty, but its ethylic salt easily reduces them. The *dibromide*, $C_{10}H_8O_3Br_2$, is soluble in ether, alcohol, and chloroform. It melts at 176° with decomposition.

Nitroaldehydecinnamic acid is freely soluble in hot water, acetone, and acetic acid. It is deposited from these solvents in prisms, melting at 194°. The *ethylic* salt crystallises in prisms, and melts at 80°.

Paraphenylenediacrylic acid, $C_6H_4(CH : CH \cdot COOH)_2$, is obtained by the action of sodium acetate and acetic anhydride on ethyl aldehydocinnamate. It is insoluble in the usual solvents, and does not melt at 310°. It forms a crystalline tetrabromide.

In the presence of sodium hydroxide, terephthaldehyde forms a condensation product with acetone, namely, *paraphenylenediacryl methyl ketone*, $C_6H_4(CH : CH \cdot COMe)_2$. Paraphenylene dilactic methyl ketone is probably formed as an intermediate product.

Leucomalachite green aldehyde, $C_{24}H_{26}N_2O$, is formed by heating an alcoholic solution of dimethylaniline and terephthaldehyde with zinc chloride for 10 hours. It melts at 143°, and yields a phenylhydrazine compound, which melts at 225°. W. C. W.

Aromatic Ketones. By K. Elbs (*J. pr. Chem.* [2], **33**, 180—188).—The following is a general method for the preparation of homologues of benzophenone:—A mixture of equivalent amounts of hydrocarbon and acid chloride is dissolved in carbon bisulphide, and the solution gradually run into a large reflux apparatus containing an equal volume of carbon bisulphide, and a weight of aluminium chloride equal to that of the acid chloride. The whole is warmed on a water-bath until the evolution of hydrogen chloride almost ceases; when cold it is gradually treated with water. It is then steam-distilled, the residue treated with very dilute hydrochloric acid, and

again steam-distilled. This is repeated, using very dilute solution of caustic soda. The ketone is then fractionally distilled. The yield of pure ketone is 50—80 per cent. of the theoretical amount. All substances and vessels employed must be free from moisture. The method works very well in the case of benzene and its homologues, but not so well with complex aromatic hydrocarbons. Those substitution products of hydrocarbons which contain halogens in the nucleus react with difficulty, and nitro-compounds do not react at all.

To reduce the ketones to secondary alcohols, 1 part of the ketone dissolved in 10—20 parts of alcohol is treated with 5—10 parts of zinc-dust and some c.c. of very concentrated potash solution, and the whole kept for some days in a warm place. The clear solution is then poured from the zinc-dust, treated with water, and the carbinol thus precipitated distilled or recrystallised. In the case of carbinols soluble in water, the alcoholic solution is treated with carbonic anhydride to precipitate the zinc and potassium as carbonates, and filtered; the carbinol is then purified by crystallisation or is distilled.

The author is investigating the action of heat or dehydrating agents on homologues of benzophenone, containing methyl in the ortho-position to the carboxyl-group, with a view to obtaining homologous anthracenes. N. H. M.

Aromatic Methyl Ketones and their Oxidation to α-Ketonic Acids. By A. Claus (*Ber.*, **19**, 230—235).—The author has previously shown (Abstr., 1885, 1136) that methyl paraxylyl ketone may be oxidised to the corresponding α-ketonic acid, paraxylylglyoxylic acid, $C_6H_3Me_2\cdot CO\cdot COOH$. He has now, in conjunction with his pupils, examined the effect of oxidation on other aromatic methyl ketones (see following abstracts).

From the results obtained he concludes: 1. That the acetyl and probably other acid nuclei when entering a conjugated hydrocarbon take, if possible, primarily the para-position to one side-group, and, secondly, the ortho-position to the smallest side-group. 2. Only those aromatic methyl ketones can be oxidised to α-ketonic acids which contain a side-group in the ortho-position to the ketone-group. L. T. T.

Oxidation of Acetophenone. By W. Strommenger (*Ber.*, **19**, 230).—All attempts to obtain an α-ketonic acid by the oxidation of acetophenone were unsuccessful, benzoic acid being invariably formed.

Paratolyl Methyl Ketone. By A. Claus and Riedel (*Ber.*, **19**, 234).—On acetylising toluene, *paratolyl methyl ketone* is obtained, together with small quantities of a compound of high boiling point, probably a condensation-product. The ketone is a colourless liquid, boiling at 220°, soluble in alcohol, ether, and benzene, almost insoluble in water. When oxidised with permanganate in the cold, it is at once converted into terephthalic acid; no α-ketonic acid could be obtained. Hydrochloric and sulphuric acids and phosphoric anhydride all cause condensation to crystalline products. L. T. T.

Metaxylyl Methyl Ketone. By A. Claus and Gärtner (*Ber.*, **19**, 230—232). *Methyl metaxylyl ketone* is prepared in a way similar to that described (Abstr., 1885, 1136) for the preparation of the para-compound. It is a colourless oil, boiling at 227—228°, and having a pleasant odour resembling peppermint. When oxidised with potassium permaganate in the cold, it yields *dimethylphenyl-glyoxylic acid*, $C_6H_3Me_2{\cdot}CO{\cdot}COOH$ [CO : Me : Me = 1 : 2 : 4] a crystalline acid, which melts at 85° to a colourless oily liquid, insoluble in water, readily soluble in alcohol, ether, benzene, &c. At about 200° this acid decomposes into carbonic anhydride and xylylaldehyde. Its salts undergo the same decomposition when boiled with bases. When boiled with dilute nitric acid, carbonic anhydride is evolved and dimethylbenzoic acid (m. p. 126°) is formed. No condensation-derivatives of the ketone could be obtained, resinous products being alone formed in all attempts. L. T. T.

Metaparadimethylphenyl Methyl Ketone. By A. Claus and Claussen (*Ber.*, **19**, 232).—*Dimethylphenyl methyl ketone*,

$$C_6H_3Me_2{\cdot}COMe\ [Ac : Me : Me = 1 : 3 : 4],$$

is a colourless, oily liquid, boiling at 243° (uncorr.). No α-ketonic acid could be obtained from this ketone; even a limited quantity of dilute cold permanganate solution oxidised it at once to dimethylbenzoic acid (m. p. 163°). On the other hand, by the action of hydrochloric acid, a crystalline condensation product of the formula $C_{20}H_{22}O$, melting at 113—114° (uncorr.), is easily formed. Phosphoric anhydride produces a second condensation product, which melts at 165°, and is now being investigated. L. T. T.

Methylpropylphenyl Methyl Ketone. By A. Claus and Cropp (*Ber.*, **19**, 232—234).—*Orthomethylmetapropylphenyl methyl ketone*, $C_6H_3MePr{\cdot}COMe$ [Ac : Me : Pr = 1 : 2 : 4], is prepared by acting on cymene with acetic chloride and aluminium chloride. It is an oil boiling at 245—250°. When oxidised in the cold with permanganate, it yields the corresponding *α-ketonic acid*, which forms a thick oil, gradually solidifying if kept in a desiccator. When oxidised with dilute nitric acid, it is partly oxidised to *cymylcarboxylic* (*paraopropyl-orthomethylbenzoic*) *acid*, but principally to the same methylisophthalic acid, $C_6H_3Me(COOH)_2$ [Me : COOH : COOH = 1 : 2 : 4], (Abstr., 1885, 1136), as was obtained by the oxidation of methyl paraxylyl ketone. The latter acid is sparingly soluble in water, and is still solid at 330°. On continued heating, partial decomposition sets in, and part of the acid sublimes. L. T. T.

Diparaxylyl Ketone. By K. Elbs and G. Olberg (*Ber.*, **19**, 408—410).—*Diparaxylyl ketone*, $CO(C_6H_3Me_2)_2$, is formed from paraxylene and carbonyl chloride in presence of aluminium chloride; it is a pale-golden viscid liquid, boiling at 325—327°, soluble in alcohol, ether, and benzene. On reduction with zinc-dust and alcoholic potash, it yields *diparaxylyl carbinol*, $CH(C_6H_3Me_2)_2{\cdot}OH$, which crystallises in colourless needles, melts at 132°, and is insoluble

in water, soluble in alcohol. The ketone yields on condensation 2 : 1′ : 4′ trimethylanthracene. V. H. V.

Intermolecular Changes in the Propyl-group. By O. Widman (*Ber.*, **19**, 273—280).—It has been shown (p. 465), that in the nitration of cumenylacrylic acid, orthonitroparapropylcinnamic acid, $NO_2 \cdot C_6H_3Pr^{a} \cdot C_2H_2 \cdot COOH$, is formed, the isopropyl-group of cumenylacrylic acid being in part transformed into the normal propyl-group. This shows that the acrylic acid-group, CH : CH·COOH, resembles the methyl-group (comp. p. 453) in exerting an influence on a propyl-group standing relatively in the para-position to it, such as tends to the formation of normal propyl.

Orthonitroparapropylcinnamic acid crystallises in globular aggregates of small needles, melts at 122—123°, and is readily soluble in alcohol and hot benzene. The results obtained on oxidation, detailed below, show that the author's first assumption that this substance was a cumenylnitroacrylic acid, was incorrect.

When oxidised with potassium permanganate in strongly alkaline solution, it yields an acid melting at about 153°, and orthonitroparahydroxypropylbenzoic acid, whilst with permanganate in weak alkaline solution or chromic acid in acetic acid solution, it yields the acid melting at 153°, and orthonitrocumic acid. When *orthonitroparapropylbenzoic acid*, $NO_2 \cdot C_6H_3Pr^{a} \cdot COOH$, the acid melting about 153°, mentioned above, is purified by recrystallisation it forms nearly colourless, rhombic tables, and when quite pure melts at 156—157·5°.

Orthamidoparapropylcinnamic acid, $NH_2 \cdot C_6H_3Pr^{a} \cdot C_2H_2 \cdot COOH$, is prepared by reducing the corresponding nitro-acid with ferrous sulphate and ammonia; it crystallises in lustrous, yellow needles, melts at 154—155°, is readily soluble in hot alcohol, and gives salts with strong acids. By long-continued boiling with dilute hydrochloric acid, it is converted into a substance crystallising in long, slender, white needles, and melting at 161—162°; this is most probably normal propylcarbostyril, but the quantity obtained was too small for further investigation.

The paper concludes with a discussion of the nature of the rearrangement of the atoms by which the change from iso to normal propyl is effected. A. J. G.

Ortho-derivatives of Cumenylacrylic Acid, and Quinoline-derivatives obtained therefrom. By O. Widman (*Ber.*, **19**, 255—268).—The author has repeated and confirmed many of the observations of Einhorn and Hess (Abstr., 1884, 1351) on the derivatives of this acid. Diacetyl-hydrocuminoïn (Roab, this Journal, 1877, ii, 894) is always formed as a bye-product in the preparation of cumenylacrylic acid by heating cumenaldehyde with sodium acetate and acetic anhydride. *Cumenylacrylic acid dibromide*,

$$C_6H_4Pr^{\beta} \cdot CHBr \cdot CHBr \cdot COOH,$$

prepared by the action of bromine vapour on the acid, forms small, white balls, melts at 190°, and is sparingly soluble in boiling benzene.

By the nitration of cumenylacrylic acid, in addition to paranitrocinnamic acid and orthonitrocumenylacrylic acid, the author has observed the formation of an acid which he first described as cumenylnitroacrylic acid (Abstr., 1885, 56), but has since found to be orthonitroparapropylcinnamic acid (see p. 464).

Orthonitrocumenylacrylic acid dibromide,

$$NO_2{\cdot}C_6H_3Pr^{\beta}{\cdot}CHBr{\cdot}CHBr{\cdot}COOH,$$

crystallises in colourless, rhomboidal tables or monoclinic pyramids, melts at 171° with decomposition, and is sparingly soluble in cold, but very readily soluble in hot benzene. The sodium salt crystallises in lustrous, white needles. When the acid is dissolved in excess of alkali, the solution allowed to remain for 24 hours and then acidified, an oil separates, which can only be solidified with great difficulty, and on analysis gives numbers agreeing with the formula $C_{12}H_{12}BrNO_4$; as the melting point is not constant (70—75°), this is probably a mixture of the isomeric *α*- and *β-monobromo*-acids. All attempts to prepare an orthonitrocumenylpropiolic acid were unsuccessful. When the dibromide is dissolved in dilute alkali, the solution heated to boiling and grape-sugar added, the diisopropylindigo of Einhorn and Hess (*loc. cit.*) is formed.

Orthamidocumenylacrylic acid, $NH_2{\cdot}C_6H_3Pr^{\beta}{\cdot}C_2H_2{\cdot}COOH$, is prepared by the action of ammoniacal ferrous sulphate on the nitro-acid. It crystallises in long, flat, lustrous, yellow prisms, melts at 165° with decomposition, and forms salts with strong acids. The *hydrochloride*, $C_{12}H_{16}NClO_2 + 3H_2O$, forms long, slender, colourless needles. The *acetyl* compound, $NHAc{\cdot}C_{11}H_{12}{\cdot}COOH$, crystallises in interlaced, slender needles, and melts at 220° with decomposition.

Hydroxyisopropylquinoline (*cumostyril*),

$$C_9NH_5Pr^{\beta}{\cdot}OH\ [Pr^{\beta} : OH = 2 : 2'],$$

is prepared by dissolving the above hydrochloride in water containing a few drops of hydrochloric acid, and gently boiling for 4 to 5 hours. It crystallises in long, slender, colourless needles, melts at 168—169°, is readily soluble in hot alcohol, sparingly in hot water, insoluble in boiling hydrochloric acid, but dissolves on gently warming with an alkali. Ether extracts the free base from the alkaline solution.

α-Chloroisopropylquinoline, $C_9NH_5Pr^{\beta}Cl\ [Pr^{\beta} : Cl = 2 : 2']$, is obtained by heating the hydroxy-compound with phosphoric chloride and oxychloride at 130—140°. It is a yellow oil heavier than water, of smoke-like odour, and can be distilled with steam, although with difficulty; it shows great indifference towards most reagents. It is nearly insoluble in water, readily soluble in ether, alcohol, and benzene. It has feeble basic properties. The *platinochloride*, $(C_{12}H_{12}ClN)_2,H_2PtCl_6$, crystallises in well-formed monoclinic prisms, and melts at 138°.

Isopropylquinoline, $C_9NH_6Pr^{\beta}\ [Pr^{\beta} = 2]$, is obtained by heating the chloro-compound with excess of an acetic acid solution of hydriodic acid. It is a colourless oil, heavier than water, and of odour somewhat recalling that of quinoline. It volatilises readily with steam. The *platinochloride*, $(C_{12}H_{13}N)_2,H_2PtCl_6 + 2H_2O$, crystallises in yellow

needles or microscopic prisms, and melts at 219—230°. The *picrate* crystallises in slender, yellow needles, and melts at 205—206°. The *chromate* forms large, well-formed, deep red prisms, and melts at about 92°. The *methiodide* crystallises in slender, yellow needles, and melts at 200°.

Orthhydroxycumenylacrylic acid, $OH\cdot C_6H_3Pr^{\beta}\cdot C_2H_2\cdot COOH$, is prepared by the diazo-reaction from the corresponding amido-acid; it crystallises in colourless, oblique tables, melts at 176°, and is very readily soluble in alcohol. A. J. G.

Oxidation-product of Orthonitrocumenylacrylic Acid. By O. Widman (*Ber.*, **19**, 269—273).—*Orthonitrocumic acid*,

$$NO_2\cdot C_6H_3Pr^{\beta}\cdot COOH\ [COOH : NO_2 : Pr^{\beta} = 1 : 2 : 4],$$

is obtained by oxidising orthonitrocumenylacrylic acid with twice the calculated quantity of a solution of chromic acid in glacial acetic acid. It crystallises in colourless, lustrous, slightly oblique tables, or in monoclinic (?) prisms, melts at 99°, and is sparingly soluble in light petroleum, readily soluble in alcohol, ether, and benzene. Potassium permanganate in the cold can also be used as the oxidising agent, but the solution must be only feebly alkaline, otherwise orthonitrohydroxypropylbenzoic acid is formed.

Orthamidocumic acid, $NH_2\cdot C_6H_3Pr^{\beta}\cdot COOH$, prepared by reducing the nitro-acid in ammoniacal solution with ferrous sulphate, crystallises in quadratic plates or long tables, and melts at 114—115°. When diazotised and boiled with water, it yields an orthohydroxycumic acid (m. p. 93—94°), undoubtedly identical with that obtained by Jacobsen by fusing carvacrol with potash, and in all probability also with that obtained by the same author by fusing sodium isocymenesulphonate with potash.

Orthonitroparahydroxypropylbenzoic acid,

$$NO_2\cdot C_5H_3(CMe_2\cdot OH)\cdot COOH,$$

is prepared by dissolving orthonitrocumenylacrylic acid (1 part) in aqueous soda of sp. gr. 1·25 (20 parts), and gradually adding concentrated aqueous potassium permanganate, the mixture being constantly agitated. It crystallises in long tables, melts at 168°, and is moderately soluble in boiling water, readily soluble in ether. When reduced with ferrous sulphate in ammoniacal solution, it is converted into the *amido-acid*, $NH_2\cdot C_6H_3(CMe_2\cdot OH)\cdot COOH$; this crystallises in colourless prisms, and melts at 158°. The ethereal solution shows a strong blue fluorescence. The *acetamido-acid*, $NHAc\cdot C_6H_3(CMe_2\cdot OH)\cdot COOH$, crystallises in slightly oblique rhombic prisms and melts at 174°.

Orthamidopropenylbenzoic acid, $NH_2\cdot C_6H_3(CMe : CH_2)COOH$ = [2 : 4 : 1], is obtained by heating orthamidoparahydroxypropylbenzoic acid with dilute hydrochloric acid, and evaporating to dryness several times with fresh quantities of dilute acid. It crystallises in golden-yellow plates, and melts at 165°. The *acetyl*-derivative melts at 122°. A. J. G.

Metanitrocumenylacrylic Acid and its Derivatives. By O. Widman (*Ber.*, **19**, 413—415).—*Metanitrocumenylacrylic acid*,

$$NO_2{\cdot}C_6H_3Pr^{\beta}{\cdot}C_2H_2{\cdot}COOH\ [C_2H_2{\cdot}COOH : NO_2 : Pr = 1 : 3 : 4],$$

is prepared by heating metanitrocumenaldehyde with acetic anhydride and sodium acetate for four hours at 170—175°. It crystallises in long, transparent, acute-angled tables, melts at 141°, is very readily soluble in alcohol and ether, and readily soluble in hot benzene. The *ethyl* salt crystallises in colourless, transparent, lustrous, rhombic tables, and melts at 58—59°. The potassium salt, the sodium salt with 3 mols. H_2O, the barium salt with 11 mols. H_2O, and the calcium salt with 3 mols. H_2O, are described.

Metamidocumenylacrylic acid, $NH_2{\cdot}C_{11}H_{12}{\cdot}COOH$, prepared by reducing the nitro-acid with ferrous sulphate in ammoniacal solution, crystallises in colourless, transparent, lustrous, six-sided tables, melts at 165°, is sparingly soluble in benzene and ether, and moderately soluble in hot alcohol; a solution in sulphuric acid becomes magenta-coloured when heated. The potassium, barium, and ammonium salts are described. The *hydrochloride*, $C_{12}H_{15}NO_2,HCl$, crystallises in colourless, flat needles; the *platinochloride*, $(C_{12}H_{15}NO_2)_2,H_2PtCl_6 + 2H_2O$, forms yellow prisms or flat needles; the *sulphate*,

$$(C_{12}H_{15}NO_2)_2,H_2SO_4 + 5H_2O,$$

crystallises in globular aggregates of plates. The acetamido-acid, $NHAc{\cdot}C_{11}H_{12}{\cdot}COOH$, crystallises in long needles and melts at 240°. The diacetamido-acid, $NAc_2{\cdot}C_{11}H_{12}{\cdot}COOH$, crystallises in microscopic needles, and melts at 236°.

Metahydroxycumenylacrylic acid, $OH{\cdot}C_{11}H_{12}{\cdot}COOH$, prepared by the diazo-reaction from the amido-acid, crystallises in colourless, concentrically grouped needles or plates, melts at 205—206°, and is nearly insoluble in water, readily soluble in alcohol.

Metanitrocumenylacrylic acid dibromide,

$$NO_2{\cdot}C_6H_3Pr{\cdot}CHBr{\cdot}CHBr{\cdot}COOH,$$

obtained by the action of bromine on the nitro-acid, crystallises in thin, colourless, rhomboidal tables, melts at 183—184°, and is sparingly soluble in boiling benzene.

Metamidocumenylpropionic acid, $NH_2{\cdot}C_6H_3Pr{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is prepared by the action of sodium amalgam on metamidocumenylacrylic acid; it crystallises in long, rectangular tables, melts at 103—105°, and is readily soluble in ether, sparingly in water. The *acetyl*-derivative, $NHAc{\cdot}C_{11}H_{14}{\cdot}COOH$, crystallises in short prisms, and melts at 168°. The nature of the propyl-group in this acid is being investigated; in the cumenylacrylic acids, it is undoubtedly isopropyl.

A. J. G.

Isopropylphenylcinnamic and Paramethylcoumaric Acids. By O. Magnanimi (*Gazzetta*, **15**, 509—513).—In this paper, a description is given of the preparation of *isopropylphenylcinnamic* and *paramethylcoumaric acids*, from isopropylphenylacetic acid with benzaldehyde and anisaldehyde respectively, by means of Perkin's reaction. The former acid crystallises in small, white needles, melting at 183°,

insoluble in cold water, very soluble in alcohol and chloroform. Its silver salt is a white precipitate slowly altered by exposure to light. The reaction which leads to its formation is as follows:—

$$C_6H_4Pr^{\beta}\cdot CH_2\cdot COOH + CHPhO = H_2O + CHPh:C(C_6H_4Pr^{\beta})COOH.$$

The second acid crystallises in minute prisms, which melt at 198°; it is insoluble in water, but soluble in alcohol and chloroform. The reaction which leads to its formation is analogous to that written above. The acid when heated above its point of fusion yields carbonic anhydride and *isopropylmethoxystilbene*,

$$OMe\cdot C_6H_4\cdot CH:CH\cdot C_6H_4Pr^{\beta},$$

which crystallises in micaceous scales, and melts at 151—152°.

V. H. V.

Methylatropic Acid. By A. Oglialoro (*Gazzetta*, **15**, 514—516).—The *methylatropic acid* described in this paper is prepared from sodium α-toluate, paraldehyde, and acetic anhydride by heating the mixture in a flask with reflux condenser for about 50 hours. Its production is probably due to the transformation of the paraldehyde into aldehyde, which reacts thus: $MeCHO + CH_2Ph\cdot COOH = H_2O + CHMe:CPh\cdot COOH$. The acid crystallises in minute prisms, melting at 135°, sparingly soluble in cold, but more soluble in hot water, soluble in alcohol and ether. V. H. V.

Preparation of Substituted Salicylic Acids. By F. W. v. Heyden (*Dingl. polyt. J.*, **258**, 380).—It is found that Schmitt's process for preparing salicylic acid (Abstr., 1885, 709) is applicable also to the preparation of substituted salicylic acids. The substituted phenates of the alkalis and alkaline earths, and more especially their halogen-derivatives, are saturated with carbonic anhydride and heated in high-pressure cylinders at 120—140° D. B.

Azo-opianic Acid and a new Indigo-derivative. By C. Liebermann (*Ber.*, **19**, 351—354).—By the reduction of nitro-opianic acid, Prinz obtained an acid of the formula of $C_{20}H_{18}N_2O_{10}$, which he termed azo-opianic acid, although at the same time he admitted that its properties were scarcely those of an azo-compound. The author points out that in the most probable constitutions suggested for opianic acid [COOH : COOH : OMe = 1 : 2 : 5 : 6 or 1 : 2 : 4 : 5], the entering nitro-group may occupy the ortho-position relatively to the aldehyde-group; in this case, the nitro-acid would yield an anthranil compound by reduction, in the same way that orthonitrobenzaldehyde yields anthranil. It is therefore proposed to halve the formula given above, and regard the substance as *dimethoxyanthranilcarboxylic acid*, $COOH\cdot C_6H(OMe)_2<\begin{matrix}CO\\NH\end{matrix}>$. This assumption of the constitution of nitro-opianic acid is proved by its yielding an indigo-derivative when condensed with acetone.

Tetramethoxyindigodicarboxylic acid, $C_{16}H_4(OMe)_4N_2O_2(COOH)_2$, is obtained as a sodium salt by heating nitro-opianic acid at 40—50° with

acetone and dilute aqueous soda. It forms a bluish-green mass, which when heated gives indigo-like vapours, and is at the same time decomposed. It is insoluble in alcohol, benzene, chloroform, and acetone, slightly soluble in acetic acid, aniline, and phenol. It is sparingly soluble in boiling water, but on addition of ammonia dissolves readily (as the ammonium salt) to a blue liquid, which gives a similar absorption spectrum to indigo-carmine. An acetic acid solution dyes wool a fine blue. Treated with zinc-dust and alkali, a yellow liquid is obtained, from which, on exposure to air, blue flocks (of the zinc salt?) separate. It dissolves in sulphuric acid to a violet-blue liquid, whose spectrum shows a sharp absorption-band from D to F; on dilution with water, it is precipitated unchanged. A. J. G.

Phthalide from Orthotoluic Acid. By E. Hjelt (*Ber.*, **19**, 412).—Phthalide is formed by the action of bromine vapour on orthotoluic acid heated at 140°.

Orthophenylenediacrylic Acid. By W. H. Perkin, Jun. (*Ber.*, **19**, 435—438).—*Orthophenylenediacrylic acid*, $C_6H_4(CH:CH\cdot COOH)_2$, is obtained by heating ethyl ortho-xylyldichlorodimalonate (Abstr., 1884, 908) with alcoholic potash for four hours on the water-bath, acidifying with sulphuric acid, &c. It forms nearly colourless flocks, does not melt at 280°, is very sparingly soluble in toluene, benzene, alcohol, carbon bisulphide, and chloroform, somewhat more soluble in acetone and water, and can be sublimed in part when heated in small quantity. The *silver* salt, $C_{12}H_8O_4Ag_2$, is obtained as a pale yellow, amorphous precipitate. When treated in alkaline solution with benzene and potassium permanganate, it yields an oil of aldehyde-like odour, possibly phthalaldehyde, as it gives phthalic acid on further oxidation. The *tetrabromide*, $C_{12}H_{10}BrO_4$, is obtained by the action of bromine vapour on the finely divided solid acid, as a powder sparingly soluble in benzene, light petroleum, carbon bisulphide, and chloroform.

Orthophenylenedipropionic acid, $C_6H_4(C_2H_4\cdot COOH)_2$, is prepared by boiling ethyl ortho-xylyldimalonate with concentrated alcoholic potash for some hours in a reflux apparatus, acidifying with sulphuric acid, &c., or by reducing orthophenylenediacrylic acid in alkaline solution with sodium amalgam. It crystallises in colourless, microscopic needles, and melts at 160—162°. A. J. G.

Incomplete Oxidation of Mellogen. By A. Bartoli and G. Papasogli (*Gazzetta*, **15**, 461—475).—The authors, in continuation of their investigations on mellogen (Abstr., 1883, 397) have studied the products of its oxidation intermediate between it and mellitic acid and the other benzenecarboxylic acids produced on its complete oxidation. Three substances were obtained by the electrolysis of nitric acid (sp. gr. = 136) with carbon poles, or by the direct oxidation of mellogen by nitric acid or alkaline hypochlorites; their formation is always accompanied by a development of heat. Amongst the products obtained were a black solid, soluble in water and alcohols, but insoluble in ether; a compound of the formula $C_{11}H_6O_9$ of acid properties, soluble in water, alcohol, and ether; and another, $C_{11}H_6O_7$, resembling

shellac in appearance, of acid properties, fusible, soluble in water, alcohol, and ether, and forming silver and barium salts of the general formula $C_{11}H_3M_3O_7$. All these substances are comparatively unstable, being readily oxidised to the benzenecarboxylic acids. V. H. V.

The Propyl-group in Thymol. By O. Widman (*Ber.*, **19**, 245—250).—Whether thymol contains a normal or isopropyl group is still an open question, inasmuch as by some reactions it yields compounds known to be normal propyl-derivatives, by others isopropyl-derivatives. The author has shown that cymidine when diazotised and boiled with water, yields thymol (Abstr., 1882, 727); it was expected that when decomposed with alcohol the diazo-compound would yield either cymene or isocymene, and thus show the nature of the propyl-group, but only resinous products could be obtained. It was then thought possible that a cymidinesulphonic acid when diazotised and boiled with alcohol might give a better result, but in this case an ethylthymolsulphonic acid was formed.

Cymidinesulphonic acid, $NH_2{\cdot}C_6H_2MePr{\cdot}SO_3H$ [Me : Pr : NH_2 : SO_3H = 1 : 4 : 3 : 6], prepared by treating cymidine sulphate with Nordhausen sulphuric acid at 160—165°, crystallises in thick, lustrous prisms, or in thin three-sided plates, or in needles. It does not melt at 260°, is sparingly soluble even in hot water, and nearly insoluble in alcohol. When suspended in alcohol and treated with nitrous acid, it is converted into the *diazo-compound;* this crystallises in very slender needles, explodes feebly when heated, and is readily soluble in water, sparingly soluble in alcohol, and insoluble in ether.

Ethylthymolsulphonic acid, $OEt{\cdot}C_{10}H_{12}{\cdot}SO_3H$, is obtained by boiling the diazo-compound with absolute alcohol as a red oil very soluble in water and alcohol. The barium salt, $(C_{12}H_{17}SO_4)_2Ba + 3H_2O$, crystallises in indistinct, white plates. As a cymenesulphonic acid could not be obtained in this way, the diazo-compound was next treated with warm hydrobromic acid, whereby it was converted into *bromocymenesulphonic acid*, whose barium salt, $(C_{10}H_{12}Br{\cdot}SO_3)_2Ba + 2\frac{1}{2}H_2O$, crystallises in very thin scales. When treated with sodium amalgam, this is converted into barium normal cymenesulphonate. From this it follows that thymol is a normal propyl-derivative, and that in its formation from cumaldehyde (*loc. cit.*), an intermolecular change of isopropyl into normal propyl must have occurred. Paterno and Spica have noticed that this change also occurs in the similar reaction by which cumyl chloride is converted into cymene. A. J. G.

Preparation of Benzidinesulphone. (*Dingl. polyt. J.*, **259**, 50.)—It has been found by the *Farbenfabriken, vormals F. Bayer und Co.*, that on heating benzidine or its salts with fuming sulphuric acid to a temperature not exceeding 120°, a new compound, benzidinesulphone, is obtained. On heating the latter with sulphuric acid above 120° and not exceeding 150°, it is converted into a sulphonic acid. *Benzidinesulphone*, $(C_6H_3NH_2)_2SO_2$, is a yellow, amorphous substance sparingly soluble in hot water. It melts above 300° without decomposition and has basic properties, forming salts with acids. The sulphate differs from the corresponding benzidine salt by its solubility in hot acidified

water, from which it crystallises on cooling in long, silky, needles. The disulphonic acid is most suitable for the preparation of dyes. To obtain this acid in one process, benzidine (1 part) is heated in a closed vessel with fuming sulphuric acid (containing 40 per cent. of sulphuric anhydride) at 100° for one hour, after which the temperature is gradually raised to 150°.

The tetrazo-compound of benzidinesulphone, similar to the corresponding derivative of benzidinedisulphonic acid, forms dyes with phenols, amines, and their sulphonic acids, which are more permanent and bluer in shade than the respective benzidine colours. Phenol, resorcinol, α- and β-naphthol, and their sulphonic acids, yield red dyes; α- and β-naphthylamine violet dyes, insoluble in water, but soluble in alcohol; α- and β-napthylaminesulphonic acid, bluish-violet dyes; whilst aniline, toluidine, xylidine, and their sulphonic acids, as well as salicylic acid, produce yellow dyes. D. B.

Base Isomeric with Benzidine obtained by passing Aniline Vapour through a red-hot Tube. By A. Bernthsen (*Ber.*, **19**, 420—425).—The products obtained in this reaction were investigated by Hofmann (*Proc. Roy. Soc.*, **12**, 383), and by Graebe, who isolated benzene, hydrocyanic acid, ammonia, benzonitrile, and carbazole; they both noticed the formation of a basic oil, but did not determine its nature. The author has reinvestigated the reaction, working on a much larger scale, and finds the basic oil to be a mixture of isobenzidine, quinoline, a colourless, oily base distilling between 300° and 360°, and giving a hydrochloride crystallising in colourless tables, and other substances.

Isobenzidine, $C_{12}H_{12}N_2$, crystallises in snow-white, iridescent plates, melts at 125°, and in general closely resembles its isomeride benzidine, from which, however, it is distinguished by the following reactions: Its aqueous solution does not react with potassium ferricyanide in the cold; it gives a grey or greyish-brown coloration, followed by a brown precipitate with chlorine-water, and its solution in carbon bisulphide gives only a slight red coloration with bromine-water. The hydrochloride, $C_{12}H_{12}N_2,2HCl$, crystallises in greyish-white plates.

Diorthamidodiphenylamine can be prepared by the action of stannous chloride and hydrochloric acid on an alcoholic solution of the corresponding nitro-compound. The *hydrochloride*, $C_{13}H_{13}N_3,2HCl$, crystallises in lustrous prisms. Attempts to convert this base into a compound of the constitution $NH<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>NH$, were unsuccessful. A. J. G.

Crystallography of Acridine-derivatives. By A. Bernthsen and A. Osann (*Ber.*, **19**, 425—427).—Methylphenylacridinium iodide forms large, lustrous, monoclinic prisms; $a:b:c = 1{\cdot}872:1:0{\cdot}79235$; $\beta = 76°\ 31'\ 20''$. The corresponding hydroxide forms triclinic crystals. Methylacridine crystallises in the quadratic system. $a:c = 1:0{\cdot}23977$; usual form $\infty P\infty$, ∞P, P. A. J. G.

β-Nitronaphthalene. By E. Lellmann and A. Remy (*Ber.*, **19**, 236—237).—The compound formerly described by Lellmann as

γ-nitronaphthylamine (Abstr., 1884, 752), appears to be orthonitro-α-naphthylamine, [$NH_2 : NO_2 = 1 : 2$]. When diazotised at 0°, and the temperature subsequently allowed to rise, *β-nitronaphthalene* is obtained. This forms small, yellow needles soluble in alcohol, acetic acid, ether, chloroform, &c.; it melts at 79°. When reduced with zinc and acetic acid, it yields the characteristic silvery scales of β-naphthylamine, melting at 112°. L. T. T.

Dinitrosonaphthalene. By M. Ilinski (*Ber.*, **19**, 349—351).—*Dinitrosonaphthalene*, $C_{10}H_6(NO)_2$, is obtained by oxidising orthonaphthalenedioxime in alkaline solution with bromine; it crystallises in long, colourless needles, melts at 127°, volatilises with steam, is insoluble in water, sparingly soluble in cold alcohol, hot light petroleum and ether, and readily in benzene. It is doubtful if this substance has an analogous constitution to Baeyer's nitrosonaphthalene, inasmuch as it shows great difference in its reactions, and is far more stable. All attempts to oxidise it further have, so far, been unsuccessful. Its investigation is being continued. A. J. G.

Action of Alkalis on Nitracetanilides and Nitracetonaphthalides. By S. Kleemann (*Ber.*, **19**, 334—340).—*Diaceto-α-naphthylenediamine*, $C_{10}H_6(NHAc)_2$, is obtained by heating α-amidacetonaphthalide hydrochloride with dehydrated sodium acetate (1 part) and acetic anhydride (4 parts). It crystallises in colourless, microscopic, double pyramids, melts at 303—304°, and is sparingly soluble in alcohol, nearly insoluble in water and ether.

Nitrodiaceto-α-naphthylenediamine, $C_{10}H_5(NHAc)_2 \cdot NO_2$ [$= 1 : 4 : 2$], is prepared by rubbing the diaceto-compound into a thin paste with glacial acetic acid, and adding nitric acid (sp. gr. 1·48) until a deep brown, clear solution is obtained, which is then poured into ice-water. It crystallises in sheaf-like tufts of very slender, yellow needles, melts at 295° with slight decomposition, is insoluble in water, sparingly soluble in cold alcohol and glacial acetic acid. When oxidised with dilute nitric acid, it yields phthalic acid. It was not found possible to eliminate the acetyl-group without at the same time the amido-groups being at least in part replaced by hydroxyl. When treated with alcoholic or aqueous potash, it dissolves to an intensely brownish-red liquid, from which nothing separates on keeping; on acidifying or treating with carbonic anhydride, the original substance separates.

Experiments with other nitracetamines show that they nearly all dissolve in alkalis, at first without alteration; they are more readily saponified than has generally been assumed, and both the solubility and the readiness of saponification depend on the relative positions of the nitro- and acetamido-groups; the greatest solubility and most ready saponification occurring where these groups are in the ortho-position; the decomposition is far less rapid with para-compounds, whilst the meta-compounds are nearly insoluble in alkalis and the decomposition takes weeks to effect. A. J. G.

α-Naphthylphthalimide. By A. Piutti (*Gazzetta*, **15**, 479—480).—The substance produced on heating phthalic anhydride with

α-naphthylamine is not, as Vanni (this vol., p. 68) supposed, α-naphthylaminephthaleïn but *α-naphthylphthalimide*, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot C_{10}H_7$; it is obtained almost in the proportion required by theory. It crystallises in prisms or rectangular laminæ which melt at 180°, and is readily converted by potash into *α-naphthylphthalamic acid*, $COOH\cdot C_6H_4\cdot CO\cdot NH\cdot C_{10}H_7$, which crystallises in pale-violet-coloured prisms; these melt at 183—185°, and are at the same time reconverted into the phthalimide. V. H. V.

The Eurhodines, a New Class of Dyes. By O. N. Witt (*Ber.*, **19**, 441—448).—The eurhodines are a class of dyes formed by the action of orthamido-azo compounds on α-naphthylamine hydrochloride and allied substances, in the same manner that paramido-azo-compounds under like conditions give indulines. When orthoparadiamido-azo-compounds (chrysoïdines) are employed, eurhodines are alone formed to the exclusion of indulines. As a type of these compounds, eurhodine, the substance obtained by the action of orthamido-azotoluene on α-naphthylamine hydrochloride, has already been described (compare Abstr., 1885, 945). It has the formula $C_{17}H_{13}N_3$, not $C_{24}H_{18}N_4$, as previously stated; its constitution is best expressed by the symbol $C_6H_3Me<\begin{matrix}N\\N\end{matrix}>C_{10}H_5\cdot NH_2$ [= 4 : 2 : 1 : 1 : 2 : 4]. The hydrochloride, $C_{17}H_{13}N_3,HCl + H_2O$, crystallises in lustrous, garnet-red needles. The nitrate is nearly insoluble in boiling water.

Eurhodol, $C_{17}H_{12}N_2O$, is prepared by heating eurhodine with moderately dilute sulphuric or hydrochloric acid in sealed tubes for three hours at 180°. It shows phenolic properties, forms a glittering yellow powder consisting of minute, dichroic crystals, can be sublimed, &c., and is very sparingly soluble in all solvents except aniline and phenol.

When eurhodine hydrochloride dissolved in absolute alcohol is heated on the water-bath, nitrogen is evolved, and a substance obtained which is probably identical with the naphthylenetoluquinoxaline prepared by Hinsberg from β-naphthaquinone and ortho-tolylenediamine (Abstr., 1885, 909).

To confirm this view as to the close relation of the eurhodines with the quinoxalines, the author has investigated the action of 1, 2, 4 triamidobenzene on phenanthraquinone, and finds that the amido-quinoxaline, $\overset{4}{N}H_2\cdot C_6H_3\overset{1,2}{<}\begin{matrix}N:C\cdot C_6H_4\\ \quad\quad |\quad |\\N:C\cdot C_6H_4\end{matrix}$, so obtained shows all the properties of a eurhodine. It is a brown glittering powder, sublimes in woolly, crystalline aggregates, and dissolves in concentrated sulphuric acid to a crimson liquid, changing to yellowish-green and again to red on dilution; the ethereal solution shows the yellow colour and green fluorescence characteristic of the eurhodines.

Eurhodines are also formed by the action of 1, 2, 4 triamidobenzene on β-naphthaquinone, benzil, isatin, diketones of the fatty series, and from polyketones such as leuconic acid. A. J. G.

Nitrosonaphthols and their Derivatives. By M. Ilinski (*Ber.*, **19**, 340—348).—*α-Nitroso-β-naphthol ethyl ether*, $OC_{10}H_6 : NOEt$, is obtained by the action of ethyl iodide on the silver-derivative of nitroso-β-naphthol; it crystallises in silky, yellow needles, melts at 50—60°, and is but little volatile with steam. When treated with alkalis, it is converted into an amorphous, grey, isomeric compound, probably a polymeride.

Orthonaphthalenedioxime-α-ethyl ether, $NOH : C_{10}H_6 : NOEt$, is prepared by boiling the preceding compound with hydroxylamine hydrochloride and alchohol in a reflux apparatus for half an hour; it forms greenish-yellow needles, melts at 153°, is sparingly soluble in alcohol, acetic acid, and benzene in the cold, and insoluble in water and light petroleum. When boiled in alkaline solution, it yields the anhydride $C_{10}H_6N_2O$, described by Goldschmidt (Abstr., 1884, 735). The potassium salt, $NOK : C_{10}H_6 : NOEt$, crystallises in brown needles. β-Nitroso-α-naphthol ethyl ether is only slightly attacked by hydroxylamine hydrochloride, Goldschmidt's anhydride being formed.

Orthonaphthalene-α-oxime-β-imide, $NH : C_{10}H_6 : NOH$, is obtained by heating nitroso-β-naphthol with aqueous ammonia at 100° for 20 to 30 minutes; it crystallises in green, prismatic needles, melts at 150—152°, and is readily soluble in the ordinary solvents except light petroleum. It shows both basic and acid properties. The hydrochloride, $C_{10}H_8N_2O,HCl$, crystallises in golden-yellow plates; its aqueous solution is dissociated on keeping or boiling. The platinochloride, $(C_{10}H_8N_2O)_2,H_2PtCl_6$, crystallises in red prisms, or with 2 mols. H_2O, in orange-yellow needles. The nitrate crystallises in large tables. The potassium-derivative, $NH : C_{10}H_6 : NOK$, is a red, crystalline powder, which dissolves in water with purple-red colour; on dilution, the free base is precipitated. When treated with hydroxylamine hydrochloride, the free base is converted into orthonaphthalenedioxime; when an alcoholic solution of the hydrochloride is mixed with excess of potassium nitrite, yellow crystals of a potassium salt, $NO{\cdot}N : C_{10}H_6 : NOK$, separate. The free nitroso-acid could not be obtained from this, as by treatment with acids a resinous mass is formed, from which hot water extracts an acid crystallising in pale-yellow needles, melting at 244° and yielding well-characterised salts.

The imidoxime when oxidised in alkaline solution is converted into Goldschmidt's anhydride; when reduced in alkaline solution with hydrogen sulphide, it yields a base crystallising in colourless scales and melting at 92—95°; the hydrochloride, $C_{10}H_6(NH)_2,HCl$, crystallises in slender needles, the sulphate in slender, white needles. This base seems not to be identical with that obtained by Koreff (this vol., p. 363) by the reduction of orthonaphthalenedioxime. A. J. G.

Syntheses of Hydroxyanthraquinones from Metahydroxybenzoic Acids and Benzoic Acid. By C. Liebermann and S. v. Kostanecki (*Ber.*, **19**, 329—331).—When 60 grams of metahydroxybenzoic acid, 120 grams of benzoic acid, 1200 grams of sulphuric acid, and 120 grams of water are heated for 10 hours at 180—200°, there are obtained about 7 grams of anthraflavic acid, 3 grams of hydroxyanthraquinone, 2 grams metabenzodihydroxyanthraquinone, 1 gram of

anthrarufin, and 1 gram of erythrohydroxyanthraquinone. The formation of dihydroxy-compounds is evidently due to the condensation of two molecules of metahydroxybenzoic acid. The separation of the individual constituents was very troublesome; the methods employed are described. A. J. G.

Synthesis of Xanthopurpurin and Purpurin. By E. Noah (*Ber.*, **19**, 332—334).—Xanthopurpurin can be obtained by heating 1 part of symmetrical dihydroxybenzoic acid, 5 parts of benzoic acid, and 25 parts of sulphuric acid for seven hours at 105—110°. When it is fused with potash, the mass dissolved in water and acidified, a precipitate of purpurin is obtained. A. J. G.

Action of Acetic Acid on Terebenthene. By G. Bouchardat and J. Lafont (*Compt. rend.*, **102**, 318—320).—When terebenthene is mixed with 3 vols. of glacial acetic acid and allowed to remain for some time in sealed tubes at the ordinary temperature, the rotatory power increases by more than 20 per cent. After six months, the excess of acid was removed by washing and the product fractionated. It contains several monacetates, the most abundant of which boils at 115° under a pressure of 10 mm., and is a neutral somewhat mobile liquid, with an odour resembling that of oil of thyme or menthol; sp. gr. = 0·9827; specific rotatory power $[\alpha]_D = -58·4$. When treated with gaseous hydrogen chloride in the cold, it yields terebenthene dihydrochloride, which melts at about 46—48°.

Another monacetate which boils at 95—105° under a pressure of 10 mm. has the same composition as the preceding compound; sp. gr. 0·9820; specific rotatory power $[\alpha]_D = 1·65$. This acetate behaves as a completely saturated compound and does not yield a hydrochloride when treated with hydrogen chloride. It corresponds with an active borneol which the authors have prepared from it.

The terebenthene not converted into acetates is materially modified, and is partly converted into a hydrocarbon, $C_{10}H_{16}$, analogous to the original terebenthene, but with a higher rotatory power, and partly into a bivalent active terpilene, with an odour resembling that of essence of citron; sp. gr. 0·86; specific rotatory power $[\alpha]_D = -62·15$. It yields a dihydrochloride, $C_{10}H_{16}$,2HCl, which melts at about 47°, and is identical with the dihydrochloride of terpilene or citrene.

C. H. B.

Monhydric Alcohols from Terebenthene. By G. Bouchardat and J. Lafont (*Compt. rend.*, **102**, 433—435).—Monhydric alcohols are obtained from the acetates previously described (preceding Abstract) by heating them for 10 hours in sealed tubes at 100° with an equal weight of potassium hydroxide and 5 to 6 times the weight of alcohol.

Terpilene acetate boiling at 110—116° in a vacuum, yields an active terpilenol which boils at 99—105° in a vacuum, or under ordinary pressure at 218—223° without decomposition; sp. gr. at 0° = 0·961; vapour-density 5·93, specific rotatory power $[\alpha]_D = -64·3$. It is a colourless, viscous, highly refractive liquid with a pungent odour recalling that of oil of mint. It is violently attacked by nitric acid

diluted with an equal volume of water, and yields acid and resinous products free from camphor: with hydrogen chloride at the ordinary temperature it forms a dihydrochloride, $C_{10}H_{16}(HCl)_2$, identical with the hydrochloride of terpilene. The mode of formation and properties of this terpilenol indicate that it is an unsaturated monhydric alcohol derived from bivalent terpilene, anhydrous terpin being the corresponding dihydric alcohol. All three compounds yield the same hydrochloride.

The acetate which boils at 95—105° in a vacuum yields a liquid which boils at 99—102° in a vacuum, and has a rotatory power of − 17° 24′. It has the composition of terpilenol, but after some time deposits crystals of camphenol, which melt at 193° and have a specific rotatory power $[\alpha]_D = - 26{\cdot}6$. If the still liquid portion is treated with hydrogen chloride, in order to remove terpilene and terpilenol, it yields a crystallisable camphenol which boils at 95—105° in a vacuum, and has a specific rotatory power $[\alpha]_D = + 13{\cdot}9$. It is evident that either the rotatory power is modified by the action of the hydrogen chloride, or the original acetate and its products are mixtures of dextro- and lævo-gyrate isomerides.

Terebenthene acetate, which boils at 105—110°, yields a mixture of terpilenol and camphenol, which contains a camphenol with the specific rotatory power $[\alpha]_D = - 43{\cdot}6$.

The different active camphenols have the same composition and properties as natural borneol; when treated with slightly diluted nitric acid at 100°, they yield an active camphor which is always lævogyrate. The opposite rotatory powers of the dextro- and lævo-gyrate camphenols are not equivalent, like those of dextro- and lævo-gyrate tartaric acid. C. H. B.

Chlorophyll. By V. Jodin (*Compt. rend.*, **102**, 264—267).—A summary of the author's earlier experiments made with a view to prove that the chlorophyllian function does not reside in the chlorophyll alone, but is dependent on the conditions under which the chlorophyll exists in the living plant (*Compt. rend.*, **61**, 192, and *Bull. Soc. Chim.*, **3**, 87). C. H. B.

Alkaloïds. By O. de Coninck (*Bull. Soc. Chim.*, **45**, 131—141).—The behaviour of the platinochlorides and aurochlorides of a large number of alkaloïds when heated with water is described. A. P.

Pyridine Alkaloïds. By O. de Coninck (*Bull. Soc. Chim.*, **44**, 617—623).—In continuation of his researches on the crude quinoline from brucine (Abstr., 1883, 740, and 1885, 273), the author finds that the fraction boiling between 150° and 170° contains a pyridine base, whose platinochloride is converted by Anderson's reaction into the double salt, $(C_7H_9NCl)_2,PtCl_2$; an intermediate salt was also obtained.

The aurochlorides of the pyridine bases, like the platinochlorides, are modified by boiling with water, but the reaction does not take place so readily nor is it so distinct.

The reducing action of the hydrides of the quinoline alkaloïds on gold chloride is so delicate and instantaneous, that it may be employed

in the fractional distillation of mixtures of the alkaloïds of this series as a means of estimating the extent to which the hydrides are present in a given fraction. A. P.

Pyridine Condensation. By C. F. Roth (*Ber.*, **19**, 360—362).—When pyridine is slowly passed through a red-hot tube, a viscid brownish-black oil is obtained, whilst part of the pyridine is carbonised and cyanogen and other gaseous products formed. The oil was fractioned, and from the main fraction (240—250°) a *dipyridyl*, $C_{10}H_8N_2$, ultimately isolated. This is a clear yellow, viscous oil, having an agreeable, peculiar, aromatic odour when heated; it boils at 280—282°, is only slightly volatile with steam, and is sparingly soluble in water, readily soluble in alcohol, ether, and chloroform. The hydrochloride, $C_{10}H_8N_2,2HCl$, crystallises in lustrous, hygroscopic needles, and blackens when heated to 200°. The platinochloride, $C_{10}H_8N_2,H_2PtCl_6$, forms clear yellow crystals; the picrate crystallises in interlaced needles, and melts at 208°. It is still uncertain whether the base is identical with either of the dipyridyls described by Skraup and Weidel. A. J. G.

Isocinchomeronic Acid. By H. Weidel and J. Herzig (*Monatsh. Chem.*, **6**, 976—988; comp. *Monatsh. Chem.*, **1**, 1).—The authors have repeated their experiments with this acid, and obtained results which leave no doubt as to the purity of the substance employed. When the ammonium salt is heated at 220—230° with acetic anhydride, 98·3 per cent. of the theoretical amount of nicotinic acid is obtained. Isocinchomeronic acid has therefore the constitution [2 : 5 or 3 : 5] previously ascribed to it (*loc. cit.*), and cannot be identical with Epstein's acid obtained from lutidine (comp. Abstr., 1885, 815 and 1078). N. H. M.

Isomeric Pyridinedicarboxylic Acids. By A. Hantzsch (*Ber.*, **19**, 289—293).—This paper is essentially a criticism of the literature of the subject, and especially of the statements of Weidel and Herzig. The author considers that the constitutions of the six pyridinedicarboxylic acids are now definitely settled, and gives the following list:—Quinolinic acid [= 2 : 3]. Lutidinic acid [= 2 : 4]. Isocinchomeronic acid [= 2 : 5]. Dipicolinic acid (Ramsay's α-pyridinedicarboxylic acid) [= 2 : 6]. Dinicotinic acid (see next Abstract) [= 3 : 5]. Cinchomeronic acid [= 3 : 4]. A. J. G.

Symmetrical Pyridinetetracarboxylic Acid and 3 : 5 Pyridinedicarboxylic Acid. By A. Hantzsch and L. Weiss (*Ber.*, **19**, 284—289).—*Symmetrical pyridinetetracarboxylic acid*,

$$C_5NH(COOH)_4\ [= 2 : 3 : 5 : 6],$$

is prepared by oxidising Engelmann's lutidinedicarboxylic acid (this vol., p. 258) with potassium permanganate. It crystallises with 1 mol. H_2O in small, lustrous needles, is very readily soluble in water, and has a strongly acid taste and reaction. The calcium salt, $C_5NH(COOH)_2(COO)_2Ca + 2H_2O$, and normal silver and copper salts,

crystallising respectively with 2 mols. H_2O and with 5 mols. H_2O, are described. Neither a hydrochloride nor a platinochloride could be obtained. When heated, it commences to lose weight at 120°, and at 150° is completely converted into the 3 : 5 dicarboxylic acid.

3 : 5 *Pyridinedicarboxylic acid* (*dinicotinic acid*) $C_5NH_3(COOH)_2$ obtained from the tetracarboxylic acid either by heating alone, or better, by boiling with glacial acetic acid, is crystalline and sparingly soluble in water, and does not melt when heated to 285°; if carefully heated between two watch-glasses, a sublimate of nicotinic acid is obtained. The hydrochloride, $C_7H_5NO_4,HCl + 2H_2O$, crystallises in lustrous needles; the platinochloride, $(C_7H_5NO_4)_2,H_2PtCl_6$, crystallises in orange-red needles. The silver and lead salts are described.

It seems very probable that the acid obtained by Riedel by heating the pyridinetricarboxylic acid formed by the oxidation of β-ethylquinoline, was in reality this dicarboxylic acid, and not, as he thought, a pyridinemonocarboxylic acid. A. J. G.

Oxidation of Isoquinoline. By S. Hoogewerff and W. A. van Dorp (*Rec. Trav. Chim.*, **4**, 285—294).—Isoquinoline (Abstr., 1883, 89) when oxidised with alkaline permanganate yields ammonia, and phthalic and cinchomeronic acids, together with traces of oxalic acid. The principal reaction is probably expressible thus: $C_9H_7N + 9O = C_7H_5NO_4 + H_2O + CO_2$, whilst the phthalic acid results from another change, $2C_9H_7N + 13O = 2C_8H_6O_4 + 2CO_2 + H_2O + N_2$; it is not, however, shown whether the nitrogen is evolved as such, or gives rise to the formation of nitrous or nitric acids. The formation of phthalic and cinchomeronic acids show that the constitution of isoquinoline is N = 2′, if that of cinchomeronic acid is N : COOH : COOH = 1 : 3 : 4, which has been independently established by Skraup's experiments. V. H. V.

Synthesis of Conine. By A. Ladenburg (*Ber.*, **19**, 439—441).—By heating a mixture of paraldehyde and α-picoline at about 250°, a small quantity of an oil of conyrine-like odour is obtained. This boils at 190—195°, is sparingly soluble in water, and on analysis gives numbers approximating to those required for an allylpyridine, $C_5H_4N{\cdot}C_3H_5$. On reduction, this substance gives a nearly quantitative yield of a base which seems to be identical with natural conine, inasmuch as it resembles it in appearance, solubility, and boiling point, and gives the characteristic double salt with cadmium iodide (m. p. 117—118°). The hydrochloride, however, melts at 203°, whilst conine hydrochloride melts at 210—211°, so that the question of identity is still not quite certain. A. J. G.

Papaverine. By G. Goldschmiedt (*Monatsh. Chem.*, **6**, 954—975; comp. this vol., p. 83).—*Papaveraldine*, $C_{20}H_{19}NO_5$, is obtained by gradually adding a 2 per cent. solution of potassium permanganate to 25 grams of papaverine, previously treated with sufficient sulphuric acid to form an acid salt and dissolved in 1 litre of water. The quantity of permanganate required is about 50 grams. The precipitate is washed with water and extracted with alcohol several times. The

yield is over 50 per cent. of the theoretical. It forms a yellowish crystalline powder, which melts at 210°, is insoluble in water, readily soluble in glacial acetic acid and in moderately dilute mineral acids; the best solvent is chloroform. When treated with concentrated sulphuric acid, it acquires a yellowish-red colour, which becomes dark violet when the solution is warmed. The *hydrochloride*, with $2\frac{1}{2}$ mols. H_2O, forms long, lustrous, slender, yellow crystals; the *acid sulphate* crystallises in long, slender, lemon-yellow needles. Both salts are decomposed by water. The *platinochloride*, with 1 mol. H_2O, forms small, lustrous, orange-coloured prisms. The *phenylhydrazine-compound* crystallises from dilute alcohol in small reddish aggregates; it melts at 80—81°.

Dimethoxycinchoninic acid, $C_{12}H_{11}NO_4 + 2H_2O$, is formed in small quantities in the preparation of papaveraldine, and is best obtained by oxidising 10 grams of papaverine with a 5 per cent. solution of 50 grams of potassium permanganate. It forms yellowish needles, which melt at 200—205° with effervescence, and is readily soluble in alcohol and hot water. The *ammonium salt* is readily soluble. The *hydrochloride* forms yellow, slender, lustrous needles; the *platinochloride* crystallises in groups of needles. An estimation of methoxyl-groups by Zeisel's method (comp. this vol., p. 493) showed that the acid contains two such groups. When boiled with hydriodic acid, and the product steam-distilled with zinc-dust, quinoline is obtained.

In the oxidation of papaverine to papaveraldine, small quantities of the following are formed besides dimethoxycinchonic acid:—α-pyridinetetracarboxylic, veratric, hemipinic, and oxalic acids, and (?) meconine.

Papaveroline, $C_{16}H_{13}NO_4$, is prepared by boiling papaverine with an excess of hydriodic acid. About half of the hydriodic acid is then distilled off, and the residue on cooling deposits crystals of the hydriodide of the new base. This crystallises from water in almost colourless small needles with 2 mols. H_2O. The free base is obtained by decomposing the hydriodide with sodium carbonate solution under a layer of ether, taking care to avoid an excess of carbonate. It forms white crystals which soon become dark when exposed to air.

When papaverine is fused with potash in a closed retort, dimethylhomopyrocatechol and methylamine distil over, whilst the residue is found to contain 3 : 4 dihydroxybenzoic acid, and a small quantity of oxalic acid.

The *phenylhydrazine-compound* of papaveric acid, $C_{22}H_{21}N_3O_6$, crystallises in bright yellow needles, melting at 190°.

The results of the experiments described in this and the preceding papers point to the following constitution for papaverine:—

$$C_9NH_4(OMe)_2{\cdot}C_6H_2Me(OMe)_2\ [Me : OMe : OMe = 2 : 5 : 6].$$

The author hopes soon to be able to determine the positions of the two methoxyl-groups in the quinoline nucleus. N. H. M.

Cocaïne and its Salts. By A. B. Lyons (*J. Pharm.* [5], **13**, 197—202).—The leaves of the coca plant do not contain more than 0·8 per cent. of cocaïne, some were found to contain as little as 0·15 per

cent. To assay the leaves, the author macerates them, finely powdered, with eight times their weight of a mixture of 95 volumes of ether and 5 volumes of ammonia; after 24 hours, the alkaloïd is separated from an aliquot portion of the liquid, dissolved in acidified water and extracted from this solution by means of ether and an alkali; the ether is then evaporated, and the alkaloïd is weighed. The leaves rapidly deteriorate in value, so that in about six months they are assumed to be worthless. The product from deteriorated leaves is always more or less coloured, and very little of it is crystallisable; that from good leaves is almost colourless and easily crystallises. Cocaïne is soluble in chloroform, benzene, light petroleum, carbon bisulphide, fused vaseline, fixed and volatile oils, and in 2000 parts of water. Cocaïne hydrochloride is not hygroscopic. It is easily soluble in alcohol, less easily in absolute alcohol and in chloroform; it is practically insoluble in ether, light petroleum, and fixed and volatile oils. The crystals from the aqueous solution contain 9·6 per cent. of water, whilst those obtained from the alcoholic solution are anhydrous. The hydrobromide crystallises readily from its aqueous solution in transparent prisms with 2 mols. H_2O, stable in the air. The citrate crystallises with difficulty and is hygroscopic. Cocaïne gives a crystalline salt with oleic acid, also with boric, sulphuric, and oxalic acids. Cocaïne in alcoholic solution when treated with potassium hydroxide is rapidly decomposed with formation of ethyl benzoate, and after a short time the solution contains benzoic acid with only traces of the alkaloïd. Lime and ammonia act similarly but more slowly. MacLagan has shown that concentrated hydrochloric acid decomposes cocaïne into benzoic acid, ecgonine, and methyl alcohol. Calmels and Gussin have shown that baryta produces the same effect, when a solution of cocaïne hydrochloride is heated with it in a sealed tube at 120°. Impure cocaïne under the action of acids frequently gives a green coloration. Mayer's reagent gives a faint turbidity in a solution containing one-millionth only of cocaïne. Iodated potassium iodide gives a rose precipitate with one part of hydrochloride in 7500 of water. Phosphomolybdic acid or tannin gives a clear precipitate with 1 part in 12,500 tannin. Caustic alkalis give a crystalline precipitate from dilute solutions; from concentrated solutions, the precipitate is amorphous at first but gradually becomes crystalline. Ammonia, alkaline carbonates, and alkaline hydrogen carbonates give amorphous precipitates which similarly become crystalline. J. T.

Cholic Acid. By F. Mylius (*Ber.*, **19**, 369—379).—The quadratic octahedral crystals of cholic acid obtained by crystallisation from alcohol do not contain $2\frac{1}{2}H_2O$ as supposed by Strecker (*Annalen*, **67**, 1), but one molecule of alcohol, and give analyses corresponding with a formula $C_{24}H_{40}O_5 + C_2H_6O$. The crystals effloresce strongly in the air. In similar manner, cholic acid crystallises from other solvents such as methyl and ethyl alcohols, and acetone combined with one molecule of the solvent. From aqueous solutions, it separates either in minute anhydrous crystals, or in rhombic tables with 1 mol. H_2O.

From bile which has been allowed to putrefy for some time, not

cholic, but choleic acid is obtained (compare Latschinoff, this vol., p. 270), together with another acid, which is named *deoxycholic* acid. The analyses of the free acid and of its barium salt point to a formula $C_{24}H_{40}O_4$. It differs from cholic acid by its ready solubility in alcohol, its sparing solubility in acetic acid, and by its taste. It may be considered to be a reduction product of cholic acid, as shown by its production therefrom by fermentation with pancreas. V. H. V.

Skeletins. By C. F. W. Krukenberg (*Zeit. Biol.*, **22**, 241—260). —The term skeletin includes a number of nitrogenous but sulphur-free substances found in the skeletal tissues of invertebrates. They are intermediate substances between carbohydrates and proteïds, and are probably amido-derivatives of carbohydrates.

The so-called proteïd reactions are not all given with equal intensity by all varieties of albuminous material. These tests were applied to the varieties of skeletin with the object of elucidating the question as to which groups of atoms in the complex proteïd molecule these various reactions were respectively due. The number of these reactions which can be applied to skeletin is small, because of the great insolubility of the various substances included under that head. *Conchiolin*, $C_{30}H_{48}N_9O_{11}$ (compare Abstr., 1885, 826) does not give the xanthoproteic, Millon's, nor the Adamkiewicz colour reactions. On decomposition, it yields leucine, perhaps glycocine, but no tyrosine. The cement substances between the eggs of various molluscs whose shells and egg capsules contain conchiolin, is coloured red by heating with Millon's reagent, and contains a body allied to keratin. *Corneïn*, $C_{30}H_{44}N_9O_{13}$, although so similar to conchiolin in its composition, differs from it by giving a red colour with Millon's test. *Spongin* does not give any of these colour reactions, and yields no tyrosine on decomposition. Conchiolin and spongin also resemble one another by yielding peptone-like substances which differ from true peptones and albumoses by not giving the three reactions mentioned above, thus differing from keratin, which is not digestible. *Fibroïn*, on the other hand, behaves to all three tests like an ordinary proteïd, and on decomposition yields leucine, glycocine, and tyrosine. W. D. H.

Hyalogens. By C. F. W. Krukenberg (*Zeit. Biol.*, **22**, 261—271). —In addition to the hyalogen present in the walls of hydatid cysts, various other allied substances occur in the animal kingdom. By the action of alkalis, these insoluble hyalogens are changed into other substances to which the generic name hyalin is given, and which are easily soluble in water. By heating them with dilute sulphuric acid, a reducing sugar, probably glucose, is formed; in this they resemble mucin.

The edible birds'-nest is chiefly composed of a hyalogen (neossine), which yields as its hyalin, neossidine. Neossine gives the xanthoproteic reaction; Millon's reaction is given by the neossine of certain birds, not by that of others. *Chondrosine* is a hyalogen obtained from the sponge *Chondrosia reniformis*. The vitreous humour from the eyes of oxen and pigs was found to contain a hyalogen, whereas the cornea did not yield one, but was found to consist chiefly of

collagen and a proteïd allied to myosine. *Spirographin*, which largely composes the skeletal tissues of the worm *Spirographis*, is also a hyalogen, but differs from the others by yielding when acted on by alkalis not only a hyalin, *Spirographidin*, but also catechol. The hyalogens are not acted on by gastric juice; some are, some are not attacked by trypsin. W. D. H.

Venous Hæmaglobin. By M. Nencki and N. Sieber (*Ber.*, **19**, 410).—The authors' statement (this vol., p. 374) that venous hæmoglobin had not previously been obtained in the crystalline form, is incorrect, the substance having been prepared by Hüfner (Abstr., 1881, 625). A. J. G.

Physiological Chemistry.

Formation of Fat from Carbohydrates in Carnivorous Animals. By M. Rubner (*Zeit. Biol.*, **22**, 272—280).—Various observers have shown that in herbivorous animals, the formation of fat from amyloïd food takes place. The present research indicates that the same may occur in flesh feeders; the dog being the animal selected for experiment, and the food given consisting of sugar and starch with a small quantity of fat, after the animal had starved for a few days.

Analyses of the food and excrements show that a large amount of carbon was retained in the body. It is proved that this would not be accounted for by the fat in the food, that the carbon would not have been assimilated in the form of glycogen, and also that the food did not remain undigested in the intestine. The conclusion is drawn, therefore, that it was stored up as fat. W. D. H.

The Formation of Hippuric Acid. By H. Tappeiner (*Zeit. Biol.* **22**, 236—240).—The hippuric acid in the urine is derived (1) from the benzoic acid in the food uniting with glycocine in the organism; (2) it is a product of metabolism of the animal tissues, and occurs in small quantities in the urine of starving animals; (3) phenylpropionic acid is one of the putrefaction-products of albumin, and it has been therefore thought that some of the hippuric acid in the urine may come from the putrefaction in the alimentary canal (Salkowski).

The present research is directed to show the actual presence of phenylpropionic acid in the alimentary canal, and thus to increase the probability of the above supposition.

The ox was the animal and hay the fodder used. The fluid part of the contents of several paunches was rendered faintly acid with phosphoric acid and distilled until volatile acids ceased to come over. The still acid residue was evaporated to dryness, and repeatedly

extracted with ether to remove the chlorophyll. An acid, yellowish-brown syrup was left, which on evaporation deposited long thin prismatic crystals of phenylpropionic acid. W. D. H.

Copper Compounds as Poisons. By Du Moulin (*J. Pharm.* [5], **13**, 189—190).—Copper sulphate to the amount of 3, 4, and 5 grams at a time was given to dogs; vomiting followed, but after some hours the animals appeared none the worse. Doses of ½—1 gram of copper subacetate were given every day for six weeks to dogs and rabbits, without producing poisonous effects. Vomiting occurred during the first four or five days, after which it ceased and did not again recur. Oxide and carbonate have been administered during a year to rabbits without hindering growth. Compounds of copper with fatty acids gave similar negative results. The author has prescribed copper sulphate in various cases of infantile sickness without producing poisonous effects. J. T.

Chemistry of Vegetable Physiology and Agriculture.

Determinations of Diastatic Action. By J. R. Duggan (*Amer. Chem. J.*, **7**, 306—312).—The determination of diastatic action by ascertaining the time required for the conversion into dextrin and sugar of a given weight of starch, using iodine as indicator, is inaccurate. The starch most suitable for determinations is arrow-root, different samples being very nearly equally acted on under like conditions. Distilled water and very carefully neutralised malt solutions must be used. The addition of very small quantities of an alkali rapidly reduces the action of diastase; the addition of very small quantities of acids at first does not retard the action of diastase, probably because of the salts contained in the starch and malt extract; a further addition of acid soon prevents the action. The action of malt extract on a neutral starch solution hardly decreases with the time of action, but with an alkaline starch solution the case is different. It is considered that the diastase is not used up in the action, and that the starch molecule splits up at once into dextrin and maltose. The action increases proportionately with increased amounts of diastase, provided the amount of starch present is also increased. H. B.

Development and Absorption of Heat by Plants. By G. Bonnier (*Compt. rend.*, **102**, 448—450).—A large number of species was employed in these experiments, and the determinations were made either with a Berthelot's calorimeter or with a Regnault's thermocalorimeter, the method of constant temperatures being adopted in the latter case.

The quantities of heat developed in unit time by the same weight of living tissues differ very considerably with the stage of development, and usually pass through successive maxima and minima. The most important maxima correspond with the commencement of germination and efflorescence respectively. These are also the stages at which respiration is most intense, but if the quantities of heat corresponding with the amount of carbonic anhydride evolved in a given time are compared with the heat actually developed during the same time, there is never any sensible agreement between the two quantities. The quantity of heat developed is not equal to that which would be produced by the combustion of the carbon lost by the organism.

At the commencement of germination, the heat actually developed is much greater than that calculated from the amount of carbonic anhydride evolved, and even greater than that which would be developed by the combination of carbon with the whole of the oxygen absorbed during germination; but after germination and during the formation and maturing of the fruit, the reverse is the case.

These facts agree with the hypothesis that the reserve substances, which are not directly assimilable, are usually formed in the organism with absorption of heat; whilst the transformation of these substances into assimilable materials is accompanied, as a rule, by a development of heat. During the consumption of the reserve substances, as at the commencement of germination, the heat developed by the transformation of these substances is added to that developed by the formation of carbonic anhydride; but whilst reserve substances are being formed, as during the maturing of the fruit, the heat actually developed is the difference between that absorbed in the formation of the reserve material and that developed by the formation of carbonic anhydride. C. H. B.

Migration of Nitrates in Plant Tissues. By G. Capus (*Ann. Agronom.*, **12**, 24—42).—The method of study adopted by the author is the microchemical one. Sections of various plant tissues were immersed in a weak solution of Arnaud's reagent, cinchonamine hydrochloride acidified with hydrochloric acid. After a longer or shorter period, according to the quantity of nitrates present, crystals of cinchonamine nitrate separate out; the size, shape, and position of the crystals, whether within or without the cell, also afford indications of the relative abundance of nitrates in the different tissues. The author's observations demonstrate that many plants have the peculiar property of storing up an excess or reserve of nitrates especially in the medullary parenchyma of the stem and in the cortical parenchyma. This reserve is greatest at the period immediately preceding the flowering; the nitrates are then stored chiefly in the lower third of the stem, and are designed for the nutriment of the physiological summit of the plant, namely, the flowering axis. If a branch containing nitrates in the stem, and showing a flowering axis, be cut off and plunged in distilled water, the nitrates soon disappear, and as they are not found in the water, must be considered to have been used by the plant. Also if a branch of this sort be cut off above the reserve

of nitrates and plunged in a $\frac{4}{1000}$ solution of potassium nitrate, sections just below the flowering products soon show the presence of nitrates. The power of accumulating nitrates is a specific property of certain cells of certain plants. Amongst those particularly rich in this reserve of nitrates are *Solanum tuberosum*, *Urtica dioïca*, *Mercurialis annua*, *Sinapis alba*, *Brassica oleracea*, *Spinacea oleracea*. Amongst those not containing nitrates in excess are *Senecio vulgaris*, *Syringa vulgaris*, *Viola tricolor*, *Malva*, *Rumex*, *Phaseolus*, and *Chrysanthemum*. Berthelot and André consider that the cells of the stem have the power of elaborating nitrates. Boussingault's opinion, which is corroborated by the author's experiments, was that the nitrates enter the plant as such from without, and are assimilated in the plant. Branches of dahlia, selected when free from nitrates, and plunged into a solution of ammonium sulphate, have never shown the formation of nitrates in their tissues. The author suggests that exhausting crops are those which possess the special property of storing up nitrates. J. M. H. M.

Composition of Unripe Potatoes. By J. Hungerbühler (*Landw. Versuchs-Stat.*, 1884, 381—388).—Asparagine, glutamine, and xanthine were obtained as components of the nitrogenous matter of the unripe potatoes. From the examination of tubers at different stages of growth, the author concludes that after a certain stage has been reached, the amount of dry matter slightly decreases, that amido-nitrogen increases but at the cost of the albuminoïd nitrogen, and that starch increases continuously whilst sugar remains fairly constant. E. W. P.

Some New Diuretics. By S. A. Popoff (*Vrach*, 1886, 74—76).—The berries and calyx of *Rubus chamæmorus*, or cloud-berry, which is used as a diuretic, do not contain any alkaloïd. When the hot alcoholic extract of a large quantity of the berries, after treatment with animal charcoal, &c., was diluted with distilled water, an acid was precipitated in light, nearly colourless flakes. This acid has marked diuretic properties, is sparingly soluble in water, easily soluble in alcohol, and forms crystalline salts with alkalis, readily soluble in water. T. M.

Manurial Value of Braken. By R. Hornberger (*Landw. Versuchs-Stat.*, 1886, 371—380).—In some districts this fern grows luxuriantly, and is used as litter; the analysis of the ash in parts per 1000 of the dry substance is as follows:—

K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3.	Mn_3O_4.	P_2O_5.	SO_3.	SiO_2.
1·32	0·66	5·79	1·81	0·40	1·32	1·21	1·07	13·50

Total ash .... 27·07 Nitrogen.... 7·06

The author has considered it necessary to give this analysis, as it differs so widely from those published by others.

There is further shown the quantities of its different constituents, which are added to a soil by employing the fern as a manure.

E. W. P.

Action of Ferrous Oxide on Vegetation. By O. Kellner (*Landw. Versuchs-Stat.*, 1886, 365—370).—These experiments were conducted in Japan with soils derived from volcanic tufa, which are rich in ferrous compounds; the iron generally appears partly as the magnetic oxide sand (to the extent of 7 per cent.), partly as easily decomposable silicate and soluble carbonate. When horse-dung was mixed with this class of soil, the decomposition of the magnetic oxide took place very slowly, and it was probable that if any harmful effects were producible by the ferrous oxide formed, the large proportion of magnetic oxide would mask those effects, as the ferrous compounds formed would be in small quantities and soon washed away by rain, or converted into the hydroxide. In 1883, experiments were made with ferrous sulphate in varying quantities, when no harmful influence on the plants in any stage of growth was remarked. The experiments would have been continued but for the publication of Griffiths' paper on the same subject (Trans., 1884, 71, and 1885, 46); the author, however, does not agree with Griffiths' views that iron sulphate is a manure, but considers that it acts indirectly in rendering the plant food soluble. E. W. P.

Analytical Chemistry.

Indicator for Weak Acids. By R. Engel (*Compt. rend.*, **102**, 214—217).—Poirier's soluble blue, C4B (Abstr., 1885, 931), can be used in the alkalimetric titration of feeble acids, and also indicates the acid function of phenols and allied compounds.

With this indicator, phenol in aqueous solution behaves like a monobasic acid, and resorcinol as a bibasic acid. An alcoholic solution of phenol, however, has no action on soluble blue previously reddened by potash, just as certain strong acids are without action on litmus in presence of alcohol. Chloral and hydrocyanic acids can be accurately titrated with soluble blue as indicator; but monhydric alcohols and ordinary aldehyde are without action on it. Polyhydric alcohols, like glycerol, show a distinctly acid reaction, and glycocine, taurine, &c., behave like acids, but these substances cannot be titrated.

Morphine, or its hydrochloride, shows distinctly a double phenolic function. C. H. B.

Permanent Potassium Iodide and Starch Solution. By C. Reinhardt (*Zeit. anal. Chem.*, **25**, 37).—To 5 grams of finely-powdered starch, thoroughly mixed with 50 c.c. of water, add 25 c.c. of potash solution (1 part solid to 2 of water). On vigorous shaking a uniform jelly is formed. Add 500 c.c. of water and 2 grams of potassium iodide and heat to boiling with constant agitation. Cool, dilute to a litre, and filter. A solution made as above, and not preserved from light, showed no trace of decomposition in a year. M. J. S.

Micro-chemical Reactions. By A. Streng (*Jahrb. f. Min.*, 1886, **1**, Mem., 49—61. Continuation of Abstr., 1885, 294).—For estimating *silver* under the microscope, the author makes use of the solubility of silver chloride in hydrochloric acid. On evaporation minute, regular crystals, mostly octahedra, of silver chloride are formed. For detecting *selenium*, the substance is dissolved in nitric acid, evaporated first alone and then with hydrochloric acid, decomposed with several drops of an aqueous solution of sulphurous acid as concentrated as possible, and allowed to stand for several hours with addition of sulphurous acid. Selenium slowly separates out in opaque granules, which may, however, be easily detected in reflected light from their reddish-brown colour. In this way, very small quantities of selenium, to 0·02 mgrm., may be detected. On treating a substance containing *sulphur* with nitric acid, and adding calcium chloride, monoclinic needles of gypsum are formed. The method proposed by Behrens for detecting sulphur may also be employed; this consists in the addition of cæsium chloride and aluminium chloride, when octahedra of cæsium alum are formed. In order to test a substance for *arsenic*, it must be oxidised with nitric acid; the presence of chlorine compounds and hydrochloric acid should be guarded against. To the arsenious acid solution, ammonia is added, then a drop of ammoniacal magnesium solution; both drops being heated, and when hot united. On cooling, ammonium magnesium arsenate separates out in rhombic crystals; the most characteristic being equilateral triangles and trapeziums, since these forms indicate the hemimorphism of the compound. For the detection of small quantities of *antimony*, the author oxidises to Sb_2O_3, adds normal barium tartrate suspended in water, and heats. On cooling, rhombic tablets of antimony barium tartrate, $Ba(SbO)_2C_8H_8O_{12} + 2H_2O$) separate out. The reaction is remarkably delicate. An excellent test for *barium* is tartar emetic, which in neutral barium solutions gives the crystalline precipitate mentioned above. Sodium phosphate is the best test for *lithium*. It should be added hot. On cooling, highly characteristic crystals are obtained.

With the aid of tests described above, the author shows that the *fire-blende* of St. Andreasberg and the *rittingerite* of Joachimsthal differ, in that the former contains antimony, and the latter arsenic. The formula of fire-blende is Ag_3SbS_3; whilst the similarity of form exhibited by rittingerite should point to the formula Ag_3AsS_3 or $Ag_3As(S,Se)_3$. B. H. B.

Method for determining Active Chlorine in Bleaching Powder. By A. Lidoff (*J. Russ. Chem. Soc.*, 1885, 555—559).—The bleaching powder is decomposed in a weighed apparatus by a 5 per cent. solution of formic acid, and the gaseous products passed first through concentrated formic acid, and then through calcium chloride, 1 mol. of carbonic anhydride being evolved for every atom of active chlorine present. A comparison of the results obtained by this method with numbers determined iodometrically, showed them to be very satisfactory. The presence of calcium carbonate in commercial bleaching powder is a source of error, this carbonate unduly raising the numbers by 0·1 to 0·5 per cent. Thus bleaching powder which

has been a long time in contact with air gives erroneous results by this method. Finally, the importance of formic acid as an anti-chlore is pointed out, the products of decomposition under these conditions being water and carbonic anhydride only; a thorough washing of the material bleached is therefore not of such importance as in the case of sodium thiosulphate. A. T.

Employment of Hydrogen Peroxide in Volumetric Analysis. —By S. Eliasberg (*Ber.*, **19**, 320—323). — Classen and Bauer (Abstr., 1883, 934) proposed a method for the gravimetric estimation of the sulphur in sulphides in which the latter were decomposed by boiling with hydrochloric acid, and the evolved hydrogen sulphide passed into an alkaline solution of hydrogen peroxide; it was thus oxidised to sulphuric acid, and was then estimated as usual. This process required the use of hydrogen peroxide free from sulphuric acid, which is troublesome to obtain. The process can, however, be converted into a volumetric one by using a carefully neutralised solution of hydrogen peroxide to which a known volume of standard alkali is added; the reaction is conducted as previously described, and at the finish the amount of alkali neutralised by the sulphuric acid formed is determined by titrating back with standard acid, using dimethylaniline-orange as an indicator. The results are accurate. The method can also be applied to the analysis of thiosulphates and tetrathionates, the salts being gently heated with hydrogen peroxide and standard alkali, &c.

Klobukoff's method of preparation (Abstr., 1885, 1110) does not yield tetrathionate free from trithionate. Sodium tetrathionate crystallises with 2 mols. H_2O. A. J. G.

Estimation of Nitrogen by Combustion. By G. S. Johnson and A. Eiloart (*Chem. News*, **53**, 76—77).—In the modification of Dumas' method already described (Abstr., 1885, 189), two boats separated by asbestos are now used instead of one boat as before. The substance is put in the front one, the chlorate in the other; it is now, therefore, possible to examine the ash of the substance and to collect with greater facility all the nitrogen due to destructive distillation before proceeding to the actual combustion.

D. A. L.

Determination of Phosphorus in Iron and Steel. By J. B. Mackintosh (*Amer. Chem. J.*, **7**, 296—306).—When iron or steel is dissolved in hydrochloric acid, a portion of the phosphorus escapes as hydrogen phosphide, a portion remains in the insoluble residue, and a portion goes into solution, but not wholly as phosphoric acid, since all the phosphorus cannot be precipitated from such solution by addition of a small amount of an oxidising agent and an acetate. All the phosphorus in the ferrous chloride solution may, however, be converted into phosphoric acid without oxidising the ferrous salt, by addition of sulphurous acid and boiling. On this the following rapid and accurate method is founded. The sample is dissolved in hydrochloric acid in a stream of oxygen or air, the escaping gases being absorbed in permanganate acidified with sulphuric acid; the solution

is heated to boiling, the passage of the oxygen current stopped, an excess of strong sulphurous anhydride solution is added to the liquid, and the boiling continued until the precipitated manganese dioxide in the absorption flasks is redissolved; the solutions are then mixed, whilst the residue is oxidised with nitric acid and potassium chlorate, and evaporated to dryness. The ferrous solution is boiled until the excess of sulphurous anhydride is expelled, a few c.c. of permanganate is added to oxidise a little of the iron, and the liquid then precipitated with an acetate, the filtrate being boiled to ensure the precipitation of the whole of the phosphorus. The precipitate so obtained is dissolved in hydrochloric acid, added to the solution of the residue, the whole evaporated to dryness to remove silica, and the phosphoric acid determined by the molybdate method. H. B.

Observations on Joly's Paper on the Titration of the Acids of Phosphorus with Different Indicators. By R. Engel (*Compt. rend.*, **102**, 431—433).—The difference between Joly's results and those which the author had previously obtained is due mainly to the fact that Joly employed very dilute solutions, in which the bi- and tri-basic salts were more or less decomposed by the water present. C. H. B.

Determination of Phosphoric Acid, Iron, and Alumina in Slags. By B. Kosmann (*Chem. Zeit.*, **10**, 52).—Basic slags contain iron phosphide, and as some of this phosphide remains associated with the silica, it requires prolonged digestion with aqua regia with renewal of the hydrochloric acid, to completely decompose it. It is pointed out that it is incorrect to calculate all the phosphorus present in such a slag as phosphoric acid without making allowance for the phosphorus as phosphide, especially when considering the technical application of the slag—Thomas-process slag, for example. Hence for the actual determination of phosphoric acid in the slag, the phosphorus from the phosphide should not be in solution. With regard to the analytical method, the filtrate from the silica is neutralised with ammonium carbonate, acetic acid added, and the whole warmed. The precipitate is thrown on a filter, washed, and dissolved in dilute hydrochloric acid, and exactly halved. In the one part, the phosphoric acid is determined, with ammonium molybdate, &c.; in the other, the iron, alumina, and their phosphates are reprecipitated, washed, dried, ignited, weighed, and the iron determined in the residue volumetrically. The phosphoric acid in the acetic acid solution is determined with uranium nitrate or otherwise. D. A. L.

The Quantitative Efficiency of the Marsh-Berzelius Method for the Detection of Arsenic. By W. P. Headden and B. Sadler (*Amer. Chem. J.*, **7**, 338—342).—The method gives satisfactory results under the following conditions:—The zinc must be free from carbon and pure in other respects. The arsenic must be present in the form of arsenious acid. Iron, copper, platinum, or their salts, and probably the other heavy metals and their salts, must be absent. The calcium chloride used for drying the gas must be neutral, and must not be used more than once. The action must be slow and

regular, and the decomposition tube kept at a dull red heat. Two decomposition tubes are necessary, about 3 per cent. of the arsenic being deposited in the second tube. H. B.

Estimation of Alkalis. By M. Kretzschmar (*Chem. Zeit.*, **10**, 195).—In order to avoid the loss which usually attends the present method of determining the alkalis, the author proceeds as follows:—After the removal of the magnesium, the hydrochloric acid solution is evaporated, and in order to ensure the complete expulsion of the hydrochloric acid, when the mass is nearly dry, it is moistened with small quantities of absolute alcohol, evaporated, and dried thoroughly at 110°. The residue is dissolved, and the solution accurately halved; in the one half the chlorine, in the other the potassium, is determined, and from the results obtained the proportions of potassium and sodium are calculated. D. A. L.

Estimation of Magnesia as Ammonium Magnesium Phosphate. By L. Briant (*Chem. News*, **53**, 99).—After adding sodium phosphate to the solution in the usual way, the author shakes it violently for ten minutes, and then proceeds at once to filter, &c. The time required for a determination is greatly shortened, and, according to the results obtained, without any sacrifice of accuracy.

D. A. L.

Determinations of Zinc in Zinc Fume. By L. Marquardt (*Zeit. anal. Chem.*, **25**, 25—29).—The coarse and fine parts are separately sampled, powdered, and mixed; 250 grams is covered with water, and then dissolved in aqua regia, adding the acids alternately. The insoluble residue, containing tin, antimony, and lead chloride, and also some zinc, is finely powdered in a mortar, and again heated with dilute nitric acid. The mixed and diluted solutions are cooled, decanted, and with the washings of the residue (using cold water) are made up to 4 litres. Of this, 8 c.c. is evaporated with a small excess of sulphuric acid, taken up with 250 c.c. of water, and mixed with excess of sodium chloride and some hydrochloric acid. Hydrogen sulphide is then passed into the liquid; the precipitate is collected, redissolved in nitric acid, and this solution again treated in the same way. The united filtrates are heated to remove hydrogen sulphide; the iron is oxidised by bromine, and the liquid is slowly poured into an excess of dilute ammonia. The iron precipitate must be redissolved and precipitated as before as often as the filtrates contain zinc. Acetic acid is added, then hydrogen sulphide, and the whole is diluted to a litre. After eight hours the precipitate is collected, washed with a mixture of acetic acid, sodium acetate, and hydrogen sulphide, dissolved in hydrochloric acid, and the zinc precipitated by sodium carbonate. The ignited oxide will contain a little silica which must be weighed after redissolving. Weighing as sulphide gives low results, owing to the formation during drying of oxide which cannot afterwards be completely sulphurised. M. J. S.

Detection and Estimation of Thallium in Presence of Lead. By E. A. Werner (*Chem. News*, **53**, 51—52).—The solution contain-

ing the two metals is neutralised if acid, and treated with sodium thiosulphate until the precipitate first formed is redissolved; potassium iodide is now added, which precipitates the thallium only. In this way, one part of thallium in 653,600 parts of solution, and mixed with over 5000 times its weight of lead, can be easily detected.

D. A. L.

Gravimetric Determination of Manganese. (*Zeit. anal. Chem.*, **25**, 114—116).—C. Reinhardt finds that from solutions containing much calcium, a little is precipitated with the manganese by Wolff's method (Abstr., 1884, 640), but considers that by a double precipitation the calcium may be completely separated. To keep out carbonic anhydride he places a soda-lime tube before the bromine flask, and adds some calcium chloride to the ammonia wash-bottle. Mathesius, for the determination of manganese in compounds containing iron, precipitates the latter from the oxidised and nearly neutralised solution by an excess of levigated zinc oxide. He then makes up to a known volume, filters, and from a measured portion of the filtrate throws down the manganese by Wolff's method, after adding much ammonium chloride and a large excess of ammonia. The precipitate is free from zinc. It is washed with solution of ammonium chloride mixed with ammonia (with which also the filter must first be moistened or the paper fibres will retain zinc), and then with hot water until all the chloride is removed. M. J. S.

Determination of Iron and Aluminium Oxides in Phosphates. By B. Dyer (*Chem. News*, **53**, 51).—To avoid regarding as iron oxide any iron pyrites which frequently is present, the phosphate is digested with hydrochloric acid, and the sand and pyrites removed in the usual manner. The solution is diluted, precipitated with ammonium acetate, the precipitate washed, dried, ignited, and weighed, and then dissolved in concentrated hydrochloric acid, citric acid is added to retain iron and alumina in solution, the whole neutralised with ammonia, acetic acid added, the lime precipitated as oxalate and determined as usual, the phosphoric acid precipitated from the filtrate as ammonium magnesium phosphate, and weighed as pyrophosphate, whilst the iron is precipitated as sulphide from the ammoniacal filtrate, and finally weighed as oxide; the alumina may be taken as difference, or, if preferred, determined. The iron present as pyrites can be easily determined by treating the ignited sand with hydrochloric acid, &c. D. A. L.

Determination of Iron and Aluminium Oxides in Phosphates. By E. W. T. Jones (*Chem. News*, **53**, 87).—The phosphate is dissolved in hydrochloric acid, and after removal of silica the solution is oxidised with nitric acid if required, and then precipitated with an acid solution of ammonium acetate. The washed precipitate is dissolved in hydrochloric acid and boiled with potash, the precipitated iron hydroxide is dissolved, reduced with stannous chloride and titrated with dichromate. The filtrate from the iron hydroxide is heated, and treated with acetic acid and ammonium acetate; the

aluminium is under these circumstances always precipitated as orthophosphate. D. A. L.

Action of Potassium Thiocarbonate on Nickel and Cobalt Salts. By T. Rosenblatt (*J. Russ. Chem. Soc.*, 1886, 30—35).—A solution of potassium thiocarbonate gives with nickel salts a dark brown, with cobalt salts a dark olive-green coloration; in concentrated solutions, precipitates of the respective thiocarbonates are formed, which are not decomposed by heating to 75°; they are soluble in water and in excess of the reagent. Hydrogen peroxide decomposes these salts, giving nickelous and cobaltic oxides and sulphuric and carbonic acids. Potassium thiocarbonate also gives precipitates with iron, chromium, aluminium, manganese, and zinc, but they are decomposed by heat: in the case of aluminium and chromium into the hydroxides, of the other metals into the sulphides.

In order to separate nickel and cobalt from mixtures containing the above-named metals, a sufficient quantity of potassium thiocarbonate and water is added to them, the liquid heated for 45 minutes on a water-bath, filtered, the precipitate washed with ammonium sulphide, the filtrate decomposed by acetic acid, and the nickel and cobalt sulphates subjected to electrolysis in ammoniacal solution.

For the qualitative detection of nickel and cobalt, the solution, if acid, is saturated with potash, a sufficient quantity of potassium thiocarbonate added, and the whole heated on the water-bath; if the filtrate has a darker colour than the reagent used, it is treated with hydrogen peroxide and the precipitate examined for nickel and cobalt. A. T.

Separation of Titanium and Aluminium, and of Titanium and Iron. By F. A. Gooch (*Amer. Chem. J.*, **7**, 283—295).—The precipitation of a sulphuric acid solution of titanium by boiling is not complete unless the solution is so feebly acid that the whole of the aluminium cannot be retained in solution. The titanium is completely precipitated by a phosphate in presence of a large amount of free acetic or formic acids, whilst the alumina is wholly retained in solution; but the method is tedious, owing to the nature of the precipitate. The quickest method is as follows:—Add to the solution acetic acid equal to from 7 to 11 per cent. by volume of the glacial acid, together with sufficient sodium acetate to convert all stronger acids present into sodium salts, boil, filter, and wash with acetic acid (7 per cent.); fuse the ignited precipitate with sodium carbonate, extract with boiling water, again fuse the residue with a little sodium carbonate, dissolve in strong sulphuric acid, and pour this solution into water, neutralise with ammonia, redissolve the precipitate in a known amount of sulphuric acid, and precipitate finally by boiling with acetic acid and sodium acetate as at first; the operations are short and easy. If a solution containing iron and titanium is treated as above, the precipitation of the titanium is incomplete; it is found best to remove the iron by passing hydrogen sulphide into the faintly ammoniacal solution of the oxides in ammonium tartrate, taking care that the solution is still ammoniacal just before filtering; the filtrate is acidified, the hydrogen sulphide expelled by

boiling, and the tartaric acid then destroyed by adding potassium permanganate to the hot solution until manganic hydroxide is abundantly precipitated; the manganic hydroxide is dissolved with help of a little sulphurous acid, and the titanium then separated by the acetate process. H. B.

Quantitative Analysis by Electrolysis. By A. Classen and R. Ludwig (*Ber.*, **19**, 323—327).—The separation of antimony and arsenic can be readily effected provided that the arsenic is present in the pentad condition. The mixture is evaporated to dryness with aqua regia, dissolved in 2 to 3 c.c. of water, an aqueous solution of 1 gram of pure soda is added together with 60 c.c. of aqueous sodium sulphide, prepared as previously described (Abstr., 1885, 932), and the operation conducted in similar manner to the separation of tin and antimony (*loc. cit.*). The deposited antimony is free from arsenic. Antimony can be separated from both tin and arsenic in this way, but if an estimation of the tin is also required, the method previously described (*loc. cit.*) must be used.

Mercury can be separated from the alkaline earths, chromium, aluminium, nickel, cobalt, iron, manganese, uranium or cadmium, by electrolysis in dilute nitric acid solution for 12 to 16 hours with a current giving 0·5—1 c.c. of electrolytic gas.

The electrolytic estimation of bismuth and its separation from zinc, nickel, cobalt, and uranium can be effected in a solution containing potassium and ammonium oxalates, by employment of a current so feeble as scarcely to give any formation of electrolytic gas in a voltameter. The metal deposited under these conditions admits of washing, &c. (Compare Classen and Reis., Abstr., 1881, 1081.)

A. J. G.

Quantitative Estimation of Methoxyl. By S. Zeisel (*Monatsh. Chem.*, **6**, 989—996).—0·2 to 0·3 gram of the substance to be examined is boiled with 10 c.c. of hydriodic acid (sp. gr. = 1·68) in a flask connected with a reversed condenser, supplied with water at 40—50°. A current of carbonic anhydride is passed through the apparatus by a tube fused into the neck of the flask containing the substance. The methyl iodide formed by the action of the hydriodic acid on the methoxyl-compound passes from the condenser through Geissler's potash bulbs containing water and a little amorphous phosphorus, heated in a water-bath at 50—60°; this serves to retain any hydriodic acid or iodine mechanically carried over. The gas then passes into two flasks, the first containing 50 c.c., and the second 25 c.c., of an alcoholic solution of silver nitrate. In 1½ to 2 hours, the whole of the iodine is precipitated as silver iodide. The alcohol is poured off from the precipitate and diluted with water when a further separation of silver iodide occurs; this is weighed in the usual way. The silver iodide so obtained is not sensitive to light.

A sketch of the apparatus and a table showing the very close results obtained by the method are given. N. H. M.

Examination of Beer, and a Method of Determining Alcohol. By E. Bohlig (*Zeit. anal. Chem.*, **25**, 19—22).—After distilling off

the alcohol, part of the residue is further distilled with an excess of magnesium hydroxide, and another part with oxalic acid. Both distillates should be free from any odour other than that of good beer wort; the former ought not to contain ammonia, and the latter should not show any opalescence. The alcohol is determined in the distillate by adding pure crystallised potassium carbonate in sufficient quantity to form a saturated solution. The alcoholic layer which separates is always of the same strength, so that the quantity of alcohol can be ascertained from its volume. A figure is given of a convenient measuring apparatus for the purpose. M. J. S.

Quantitative Estimation of Glycogen. By R. Külz (*Zeit. Biol.*, **22**, 161—194).—Two methods have hitherto been adopted for the estimation of glycogen in liver and muscle; the first consists in prolonged extraction with hot water, the second with hot potash; from the solutions so obtained the proteïds are precipitated by hydrochloric acid and potassio-mercuric iodide, and then the glycogen by alcohol; the precipitate so obtained is collected, dried, and weighed. A point about which previous observers disagree, is whether in the latter method, the potash causes any change in the glycogen. To this question, and also to the question which of the two methods is the better, the present research is directed. The conclusions arrived at are as follows:—

(1.) The method of extraction by potash is much quicker than that by water, and requires less apparatus.

(2.) With liver it gives as good, and with muscle better, results than the water method, as it extracts the glycogen more thoroughly.

(3.) The potash causes no change in the glycogen when employed to extract it from these tissues, although, when potash is boiled with a solution of pure glycogen, it is found to cause a loss of from 6 to 10 per cent.

(4.) In an artificial mixture of solution of glycogen and white of egg, the precipitate of mercury albuminate carries down with it about 12 per cent. of the glycogen, which is not separated from it by prolonged and careful washing; but no such loss occurs during the similar precipitation of proteïd in a potash extract of liver or muscle. W. D. H.

Almond Oil Testing. By G. Vulpius (*Arch. Pharm.* [3], **24**, 59—64).—The author examined the *elaïdin* test, employing for that purpose samples of genuine almond oil obtained from a respectable firm of dealers; oil pressed by himself from both sweet and bitter almonds; and the same oils mixed with known quantities of olive oil. The test was applied in three ways:—(*a*) Fifteen parts of oil were shaken up with a mixture of three parts of fuming nitric acid and two parts of water; (*b*) the same, with the addition of a fragment of copper; (*c*) equal volumes of oil and the acid mixture given in (*a*). The investigations show that the test gives very variable results, and confirms the assertions of Kremel and others, that it is not easy to found a satisfactory method upon it. J. T.

Detection of Acetone in Pathological Liquids. By P. Chautard (*Bull. Soc. Chim.*, **45**, 83—86).—The presence of acetone in urine or pathological liquids may be readily detected by adding a drop of an aqueous solution of magenta decolorised by sulphurous acid to the suspected liquid, when, if acetone is present, a violet colour is produced, the intensity of which is proportional to the amount present. In dilute solutions, the coloration does not appear until after four or five minutes; if the amount of acetone is very minute, 200 c.c. of urine may be distilled at a gentle heat, and the first 15 c.c. which pass over examined; by this means, the presence of less than 0·01 per cent. of acetone may be detected. A. P.

Natural Fats. By C. Dubois and L. Padé (*Bull. Soc. Chim.*, **44**, 602—608).—The authors have determined the solubility of butter, lard, veal fat, beef fat, mutton fat, and margarin in absolute alcohol, acetone, ether, and amyl alcohol. They find that the percentage of butter may be readily determined in an adulterated sample by estimating the solubility in alcohol of the mixed fatty acids prepared from it. A table of the solubilities in alcohol of mixtures of from 5 to 95 per cent. of butter with the above fats is given. The addition of only 5 per cent. of veal fat (which adulteration has the least marked effects) may be readily detected by this method. A table of the melting points of the fatty acids prepared from mixtures of butter with other animal fats is also given, and may serve as a useful control on the solubility determinations. A. P.

Melting Points of Fats. By C. Reinhardt (*Zeit. anal. Chem.*, **25**, 11—19).—The great discrepancies in the published accounts of the melting points of fats indicate that the methods employed are not free from sources of error. The author recommends a modification of Guichard's method. A glass tube of the same thickness as the walls of the thermometer bulb is plunged into the melted and filtered fat so as to fill its end with a solid plug of the fat of the same length as the thermometer bulb. After a day or two (comp. Lenz, *ibid.*, **23**, 568), the tube is connected with a vessel containing air under a definite pressure, and the end containing the fat is then heated as usual in a vessel of water, with the thermometer bulb on a level with the fat cylinder. The temperature is taken at the moment when the fat is driven out of the tube by the air pressure. The result is influenced both by the diameter of the tube and by the amount of the air pressure. M. J. S.

Santonin Estimation. By F. A. Flückiger and J. Ehlinger (*Arch. Pharm.* [3], **24**, 1—11).—To determine the amount of santonin in the plants in which it occurs, the following method was finally adopted:—5 parts of raw material mixed with 1 part of slaked lime were boiled a couple of hours with a considerable amount of alcohol of sp. gr. 0·935. After allowing to cool, the liquid was poured off, and the boiling was repeated twice at least with fresh alcohol, after which the whole of the alcohol was distilled off from the clear solution. The residual liquid was saturated in the cold with carbonic

anhydride, filtered after some hours, and the filtrate evaporated to dryness. The residue was then ground up with animal charcoal and alcohol of the strength given above, and digested with a measured quantity of alcohol. After boiling up, the liquid was passed through a filter, the residue was washed with hot alcohol, and the alcohol expelled from the filtrate, yielding a liquid in which santonin crystals appeared after some hours. One sample of *Flores cinæ* thus treated gave 1·82, 1·88, and 1·92 per cent. of santonin; further, 20 grams of an exhausted sample of worm-seed, to which 0·30 gram of santonin was added, yielded 0·29 gram of santonin. Santonin occurs only in the parts of the plant above ground, not in the dry, woody root. J. T.

Investigation of Tannins. By F. Nötzli (*Dingl. polyt. J.*, **259**, 177—188, 228—239, and 272—284).—After some introductory remarks on the preparation and chemical constitution of the tannic acid of oak-bark, the author gives an outline of the different methods proposed for estimating the tannin in barks and other tannin materials. He then discusses at some length the methods recommended by Löwenthal, Simand, and Procter, and as an outcome of his researches describes a modified method for estimating tannins. The process involves the use of (1) a permanganate solution containing 1 gram of potassium permanganate per litre, standardised with iron or oxalic acid; (2) a solution of indigo prepared by dissolving 125 grams of indigo-carmine paste in 6 litres of water, adding 400 c.c. of concentrated sulphuric acid, and filtering the mixture; (3) a gelatin solution, 20 grams per litre, to be prepared every day, as it decomposes very rapidly; (4) dilute sulphuric acid, 1 kilo. per 10 kilos. of water; (5) pure sodium chloride; and (6) kaolin. To effect the titration, 10 c.c. of extract of bark (or 5 c.c. in the case of rich barks) is transferred to a large porcelain basin and treated with 20 c.c. of indigo solution and 1 litre of water. The permanganate solution is then added gradually (about three drops in two seconds), the mixture being stirred continually. The end of the reaction is ascertained by the change of colour from light green to pure yellow. At this stage the edge of the basin exhibits a reddish tinge, the appearance of which indicates the completion of the oxidation. To analyse barks, the author proceeds as follows:—10 grams of the bark previously dried at 100° are boiled out repeatedly with water until iron paper ceases to give a reaction indicative of tannin. The infusion is then made up with water to 1 litre, and a portion filtered through a dry filter-paper; 5 or 10 c.c. of the filtrate is now titrated with permanganate. 50 c.c. of the filtered extract is precipitated with gelatin, salt, and kaolin, and 10 or 20 c.c. of the filtrate titrated. The permanganate values obtained are calculated into percentage of tannin contained in the bark according to Neubauer's equivalent, 63 oxalic acid = 41·57 tannin. D. B.

General and Physical Chemistry.

Refraction of Fluorine. By G. Gladstone (*Phil. Mag.* [5], **20**, 481—483).—From a review of all the determinations of the refractive indices of fluorine compounds, the author shows that the refraction equivalent of fluorine must be very low, varying from 0·3—0·8, the results obtained with different substances being very discordant. The specific refraction of fluorine, therefore, can scarcely be more than the half of that of any known substance, and will lie between 0·015 and 0·044. A. J. G.

Sensitising Action of Dyes on Silver Chloride and Bromide. By J. M. Eder (*Monatsh. Chem.*, **7**, 1—8).—For these experiments silver chloride gelatin plates, with ferrous oxalate or citrate developer, and silver bromide plates with alkaline developer, were used. Both were immersed in baths of different dyes (generally 1 : 20000), and thus sensitised for the least refractive rays. Daylight and gaslight (Argand burner) were employed as sources of light, and Warnecke's sensitometer was used for photometric measurements. The following results were obtained:—

	Gaslight.	Daylight.
Sensibility of ordinary chloride plates	1·0	1·0
„ chloride plate + 1 : 20000 eosin	1·3	0·3
„ „ + 1 : 80000 eosin	1·7—2·1	0·6—1·0
„ „ + 1 : 20000 cyanin	1·7	0·3—0·5
„ ordinary bromide plate.....	50	5
„ bromide plate + 1 : 30000 eosin	60—120	4—5
„ „ + 1 : 20000 cyanin	45—55	2—3

Naphthol-blue reduces the sensibility. Eosin and cyanin have a greater sensitising action on chloride plates in the presence of ammonia than without it; ammonium carbonate and sodium hydroxide exert a retarding influence compared with ammonia. A much more intense photographic image is obtained with equal exposures in the presence of dyes than in their absence; and the negatives obtained in the former case are free from halos or irradiation effects. The colour of the film of reduced silver is also influenced by the presence or absence of dyes. G. H. M.

Determination of Boiling Points of Small Quantities of Liquids. By A. Siwoloboff (*Ber.*, **19**, 795—796).—A drop of the liquid is put into a glass tube which has been drawn out and fused together at the end. Into this tube is inserted a capillary tube fused together just above the lower end. The whole is then put, together with a thermometer, into an ordinary melting point apparatus. As soon as a quick stream of bubbles rises from the end of the capillary tube the temperature is observed. This must be repeated a few times, and the mean result taken.

The capillary tube is used to prevent the liquid from becoming superheated. A sketch of the apparatus is given. N. H. M.

New Law in Thermochemistry. By G. F. Becker (*Amer. J. Sci.*, **31**, 120—125).—Berthelot's thermochemical law applies only to the final molecular configuration of given substances, and gives no information as to the series of transformations which they undergo before reaching a condition of stable chemical equilibrium. The *rate* at which chemical energy is converted into heat by various possible reactions, appears to be an important factor in determining the order of their occurrence. To determine experimentally the rate at which this heat is produced was out of the question with the time and resources at the author's disposal. He therefore undertook to inquire whether, by considering chemical energy as a form of motion, any definite results could be reached as to the rate of the evolution of heat. This investigation eventually led to a principle embracing that sought. This is published under the title of a "Theorem of Maximum Dissipativity" (*Amer. J. Sci.*, **31**, 115—120). The chemical interpretation of this principle is:—The sum of the chemical and physical transformations in any chemically active system will be such as to convert higher forms of energy into heat, light, &c., at the greatest possible rate, provided that the interval of time for which the comparison is made is a multiple of a certain fraction of the period of the most rapidly moving particles of the system. For all experimental purposes this is equivalent to the statement that the transformations will be such as to evolve heat or light at the highest possible rate. This law obviously includes Berthelot's. In conclusion, the author points out the applicability of this law to the determination of the order of the genetic succession of minerals in massive rocks.

B. H. B.

Extension of the Law of Density Numbers to a Case in Thermochemistry. By J. A. Groshans (*Ber.*, **19**, 497—499).—The molecular heats of combustion (Q) of paraffins and olefines can be calculated according to the formula $Q = 33333\frac{a}{n} \cdot \frac{q}{2}$, in which $a =$ the molecular weight, and $n = q + p$, the number of atoms of hydrogen and carbon respectively in the compound. The heat of combustion of hydrogen being assumed to be 33333, instead of 34000, the observed figure.

In the general form $Q = 33333\frac{a}{n}x$, this formula can be applied to other series of compounds, the value of x varying in different series: with the fatty alcohols and ethers $x = \frac{q}{2} - 1$.

The heat of formation of the paraffins can be calculated according to the formula $H = 35220\frac{a}{n} \cdot \frac{q}{2}$.

A. J. G.

Expansion of Ether at Various Pressures. By G. P. Grimaldi (*Gazzetta*, **15**, 517—527).—The author has determined the coefficient of expansion of ether in the liquid state for every 10 degrees from 0° to 100°, under pressures varying from 1 to 25 metres, and from the results

deduced the values for $\frac{dp}{dt}$. As a general result it follows that ether at high pressures has a maximum density at temperatures which vary with the pressure. Comparing the values obtained with those deduced from the formulæ proposed by Dupré, van der Waals, and Mendeléeff, it appears that the formula $\frac{l_1}{l} = \frac{V-b}{V}$ of van der Waals gives satisfactory results. In this formula l_1 is the mean path-length of the molecule, l the path-length if the molecule were a material point and not of sensible dimensions, and b some multiple of the specific molecular volume, 8 according to Blaserna, and 4 according to van der Waals. V. H. V.

Influence of Temperature on the Heat of Dissolution of Salts. By W. A. Tilden (*Proc. Roy. Soc.*, **38**, 401—414).—Experiments, quoted in this paper, were made with a view of throwing some light on the condition of a solid when dissolved in a liquid, especially in cases which display a critical temperature of solution, such as that of sodium sulphate. The data obtained show that although the original method of preparation of the anhydrous salts influences the result, yet in all cases the heat-change is more exothermic or less endothermic with increase of the temperature at which the salt is dissolved. The result is in accordance with the *à priori* principle first enunciated by Person, more fully examined by Berthelot and Thomsen, and embodied in the equation $Q_T = Q_t + U - V$. In this, Q_T and Q_t are the heat-changes in the dissolution at temperatures T and t respectively, U the sum of the heat-capacities of salt and water, and V the heat-capacity of the solution between the above limits of temperature. In all cases investigated, however, whether exothermic or endothermic, the observed results were less than those calculated from this formula; or, expressed in words, there is consumption of energy corresponding to an absorption of heat, unaccounted for by the difference of the specific heats of salt and water, taken separately, and of the resultant solution.

The net thermic result is the effect of the mixed causes; on the one hand are the liquefaction of the salt and its intermixture with the solvent, both being endothermic changes; on the other hand is the exothermic change of chemical reactions between the salt and water. These reactions, evidenced in the case of the salts of the heavy metals by the formation of insoluble hydroxides or basic salts, are probably not altogether without effect in salts of the alkali metals; a part of the difference between the observed and calculated results is doubtless to be accounted for by this decomposing action of water.

V. H. V.

Dissociation of Liquids. By H. W. B. Roozeboom (*Rec. Trav. Chim.*, **4**, 355—361).—The experiments of Debray, Isambert, and others, on the dissociation of solids have differentiated two phenomena, the one discontinuous, in which the constancy of tension of the gas evolved at any particular temperature points to the coexistence of decomposed and undecomposed molecules; the other continuous, in which

the variability of the tension and its diminution, with the quantity of gas contained in the combination, points to a uniform diffusion of gaseous among solid particles. The constancy of dissociation tension thus offers an important criterion between chemical combination and mere solution. As experiments hitherto have been restricted to cases in which a gas is evolved from a solid, the author has investigated cases in which the products of dissociation are a gas and a liquid, particularly the dissociation of the compound $NH_4Br,3NH_3$, an instance of chemical combination, and of the mixtures of chromium oxychloride with chlorine, and of bromine with nitric oxide, which are found to be cases of mere solution. (Compare following Abstracts.)

V. H. V.

Dissociation of Compounds of Hydrogen Bromide with Ammonia. By H. W. B. Roozeboom (*Rec. Trav. Chim.*, **4**, 361—379).—Troost (Abstr., 1881, 972) has described the preparation of two compounds of hydrobromic acid with ammonia, one, NH_4Br,NH_3, a solid, the other, $NH_4Br,3NH_3$, melting at + 6°. The author has more fully examined the dissociation tension of these two compounds; he finds that the latter compound melts at 8·7° in closed vessels, but on decreasing the proportion of ammonia from 3 mols. NH_3 to 2·63 mols., the point of fusion is lowered to 6·6°. The phenomenon is analogous to the formation of the so-called cryohydrates, the compound $NH_4Br,3NH_3$ being comparable to ice, and the compound NH_4Br,NH_3 to a saturated saline solution.

From the experiments on the dissociation tension both of the liquid and at the point of fusion of the solid compounds, the following conclusions are drawn: (1) The tension of the liquids decreases regularly with decrease in the proportion of ammonia; (2) the tension of the compound $NH_4Br,3NH_3$ in the solid state remains constant for the same temperature, whatever be the amount of dissociation; (3) the tension of the solid compound is less than that of the liquid, but as the former increases more rapidly with the temperature than the latter, they ultimately become equal; namely at the point of complete fusion of the combination $NH_4Br,3NH_3$. Finally to each composition of the liquid a certain temperature corresponds, below which the dissociation tension remains constant for the same temperature, and that whatever the quantity of ammonia expelled, thus pointing to the formation of a heterogeneous system. The experiments described are illustrated by a series of curves of dissociation tension in terms of temperature, that of the combination NH_4Br,NH_3 being continuous, whilst that of the combination $NH_4Br,3NH_3$ exhibits a point of inflection corresponding to its point of fusion.

V. H. V.

Solubility of Chlorine in Chromium Oxychloride. By H. W. B. Roozeboom (*Rec. Trav. Chim.*, **4**, 379—381).—It is well known that in the preparation of chromium oxychloride a liquid is obtained, which contains a considerable proportion of free chlorine. Experiments are quoted in this paper to show that the proportion of chlorine varies *continuously* with the temperature and pressure. The phenomenon is, therefore, one of solution.

V. H. V.

Solubility of Nitric Oxide in Bromine. By H. W. B. Roozeboom (*Rec. Trav. Chim.*, **4**, 381—383).—According to experiments of P. Muir, the liquid $NOBr_3$ on dissociation exhibits certain points of constant composition under different pressures (this Journal, 1875, 844). The experiments of the author, however, show that the tension of nitric oxide varies continuously when the composition of the substance varies from $NOBr_3$ to $NOBr_4$; between these points, therefore, the nitric oxide is merely dissolved in the bromine.

V. H. V.

Dissociation of the Hydrate of $HBr,2H_2O$. By J. H. van't Hoff (*Rec. Trav. Chim.*, **4**, 414—417).—It has been shown by Roozeboom that the curve of tension of dissociation of solution of the hydrate of hydrobromic acid, $HBr,2H_2O$, expressed in terms of temperature, exhibits three points of inflection. One corresponds with a point at which the acid and water are in the molecular ratio $1HBr : 2H_2O$, whilst at lower pressures the quantity of acid is less, and conversely at higher pressures more than is required for this ratio. In this paper, the author demonstrates that the second point of inflection at $-15{\cdot}5°$ and $2\frac{1}{2}$ atmos. is that at which the heat of transformation of the hydrate $[2H_2O,HBr, \text{solid} = 2H_2O,HBr_{(1-n)} \text{ liquid} + nHBr]$ is zero, whilst below and above this temperature there is an absorption and evolution of heat respectively. V. H. V.

Limited Hydration of Ammonium Carbamate. By H. J. H. Fenton (*Proc. Roy. Soc.*, **39**, 386—393).—The hydrolysis of ammonium carbamate affords a simple example of a chemical change, occurring in solution in which two molecules combine to form one more complex, $NH_2{\cdot}COONH_4 + OH_2 = CO(ONH_4)_2$. It has been shown by the author (Trans., 1879, 12) that ammonium carbamate when treated with sodium hypochlorite and hydroxide yields half its nitrogen as such, whilst the other half remains in the form of sodium carbamate, which in its turn can be decomposed by sodium hypobromite. Since then, by the former reaction, the nitrogen existing in the form of ammonium only is evolved as such, any excess of nitrogen beyond the quantity evolved is an index of the amount of water assimilated in the process of hydrolysis, which may be expressed simply in terms of the ratio of the number of molecules of water thus assimilated to that of the molecules of ammonium carbamate taken. Experiments are quoted to show the influence of various conditions such as time, mass, and temperature; the reverse action or conversion of the carbonate to carbamate is also studied. From the results, it is shown that the change proceeds at first rapidly, becoming gradually slower, and finally reaches a limit short of complete hydrolysis, the time required decreasing as the relative number of molecules of water increase. *Secondly*, the amount of hydrolysis is a function of the number of water molecules present, the minimum change occurring when the salt and water are present in about equimolecular proportions. This system is analogous, therefore, to the combination of hydrogen with iodine, investigated by Lemoine, and of phosphorus trichloride with chlorine. *Thirdly*, the amount is less the lower the temperature; at a sufficiently low temperature it is probable that the hydrolysis will be *nil*.

Conversely, it is shown that normal ammonium carbonate is reconverted into the carbamate, the degree of this conversion being greater the less the relative number of water molecules.

In conclusion, a few remarks are added on the quantitative estimation of carbamide, carbamic acid, and ammonia, when present together in the same solution, by means of the sodium hypochlorite and hypobromite reactions. V. H. V.

Influence of Neutral Salts and of Temperature on the Inversion of Cane-sugar by Acids. By J. Spohr (*J. pr. Chem.* [2], **33**, 265—284).—In continuation of his experiments on this subject (Abstr., 1885, 1181), the author finds that when the relation between the amount of acid and water present is constant, but the amount of the cane-sugar variable, different weights of the sugar are inverted in equal times. The intensity of the inverting action of hydrochloric or hydrobromic acids always increases with the amount of neutral salts added, this increase being greatest when the amount of the neutral salt present is relatively small compared with that of the acid, and least when the neutral salt is in relatively large proportion. If the amount of acid present is constant, the increase of the rate of inversion is directly proportional to the amount of the neutral salt added. The amount of the neutral salt present being constant, the intensity of the inverting action of the acid varies directly with its concentration. In the case of acids similar to hydrobromic acid, the percentage of alteration of the rapidity of the inversion caused by the addition of a neutral salt depends only on the quantity of the added salt, and is independent of the concentration of the acid. The results obtained by the author when employing hydrochloric acid are similar to those obtained with hydrobromic acid, and do not support the views adopted by Löwenthal and Lenssen. The laws according to which the intensity of the inverting action of sulphuric acid is affected by the concentration of the acid and presence of the neutral salt are much more obscure than is the case with the monobasic acids; this is partly due to the formation of double salts; the neutral salts, however, act more markedly when the amount present is relatively small compared with the amount of acid. A. P.

Retardation of Chemical Change. By J. J. Hood (*Phil. Mag.* [5], **20**, 444—456).—In a previous paper, the author has shown that the rate of oxidation of ferrous sulphate by potassium chlorate is decreased by the presence of various sulphates; and that the degree of such retardation is dependent on the quantity and nature of the sulphate added. As the number of sulphates which can conveniently be used is comparatively small, the effect of chlorides on the oxidation of ferrous chloride with potassium chlorate was studied, and as a result it is shown that no two chlorides give the same retardation effects, the presence of potassium and ammonium chlorides decreasing the rate of chemical change; magnesium, zinc, and cadmium chlorides increasing the rate; whilst sodium chloride practically produces no effect. Regarding these results, it is difficult to understand the different effects produced by such similar kinds of matter

as sodium and potassium chlorides, if the decrease of rate of change caused by the presence of chemically inactive substances in the system results from the diminution of the possible number of molecular impacts of the active substances in a given time and under given conditions.

As to the influence of the presence of sulphates on the system, ferrous chloride, potassium chlorate, and hydrochloric acid, it is observed that equal weights of ammonium, sodium, potassium, and lithium sulphates produce equal retardation effects; whereas zinc, magnesium, and cadmium sulphates all produce per unit-weight different effects. V. H. V.

The Periodic Law. By T. Carnelley (*Phil. Mag.* [5], **20**, 259—268; and 497—514).—In these papers it is shown that the four following classes of compounds—(i) the elements with the halogens, (ii) the elements with the hydrocarbon radicles, (iii) the hydrocarbon radicles with the halogens, and (iv) the hydrocarbon radicles with one another, exhibit similar periodic variations in their physical properties, such as melting and boiling points and specific gravities. Nine general relations between the physical constants are given and illustrated by a series of tables; the following are the more important:—(i) If the elements, or isologous series of hydrocarbons, be arranged in the order of their atomic weights, the melting and boiling points rise and fall periodically; in the former class, under similar conditions, the specific gravities diminish up to the middle term and then increase to the last member of the series.

(ii) In the case of the elements, the boiling point increases and the specific gravity diminishes as the molecular weight of the hydrocarbon radicle increases; the melting and boiling points of the halogen or alcoholic derivatives of a hydrocarbon radicle increase with increase of atomic weight of the halogen or molecular weight of the hydrocarbon radicle.

(iii) The boiling points and specific gravities of the alcoholic compounds of any one group of analogous elements increase as the atomic weight of the element increases; similarly in any group of homologous hydrocarbons, the melting and boiling points of the halogen or hydrocarbon-derivatives increase as the molecular weight of the hydrocarbon radicle increases.

(iv) These differences between these various physical properties are algebraical. The periodic variations are illustrated by a series of tables; the number of exceptions do not exceed 5 per cent., many of which can probably be accounted for by single errors in the original data. V. H. V.

Isodimorphism. By S. Rideal (*Ber.*, **19**, 589—591).—A comparison of the specific volumes of arsenious and antimonious anhydride in their two forms shows—(1) that the specific volumes of the octahedra are greater than those of the prisms; (2) that the difference in the specific volumes of the two modifications is almost the same in each case; (3) that the difference between the specific volumes of the octahedra is almost the same as in the case of the prisms; (4) that these differences are very small compared with

the specific volumes; (5) that arsenic and antimony, which are homöomorphous in the free state, are isomorphous in both forms of their trioxides. Similar results are obtained in comparing stannic and titanic oxides. Hence it is concluded that isodimorphous substances have not identical, but only analogous specific volumes.

The specific volumes of the dioxides of titanium, zirconium, tin, and thorium in the quadratic form (compare Nordenskjöld, *Ann. Phys. Chem.*, **110**, 642, and **114**, 612) increase with the atomic weights:—

	TiO_2.	ZrO_2.	SnO_2.	ThO_2.
Specific volumes....	19·8	20·14	22·35	28·7

These numbers show the near relation of tin to the other elements, and further, that the atomic weight of thorium requires revision.

N. H. M.

Hypothesis of Interchangeable Union. By C. Laar (*Ber.*, **19**, 730—742).—This paper deals with the classification of the numerous substances now known which exhibit reactions too divergent to be accounted for by any single structural formula for each substance, and thus point to a ready migration of the atoms in certain groups occurring in such compounds.

Inorganic Chemistry.

Action of Potassium Permanganate on Thiosulphuric Acid. By M. Hönig and E. Zatzek (*Monatsh. Chem.*, **7**, 48—52).—Gläser (Abstr., 1885, 957) stated that neutral solutions of thiosulphates are completely oxidised by potassium permanganate, and that Hönig and Zatzek were in error in stating that complete oxidation took place only in alkaline solutions. The authors have re-examined their work and maintain their original statement. When neutral solutions are boiled with permanganate in excess, sulphur always remains in solution after precipitating the sulphuric acid formed with barium chloride; this is oxidised to sulphuric acid on addition of bromine. When, on the other hand, an alkaline solution of thiosulphate is boiled with excess of permanganate, the whole of the sulphur can be removed as barium sulphate, and no more sulphuric acid is obtained by adding bromine. They also conclude that the composition of the precipitated manganite cannot be relied on to indicate the nature of the decomposition, as the precipitate has no constant composition.

G. H. M.

Amount of Carbonic Anhydride in the Air. By W. Spring and L. Roland (*Chem. Centr.*, 1886, 81—83).—Previous determinations of the amount of carbonic anhydride in the air, and Schulze's and Schloesing's theory that the constant amount depends on the bicar-

bonate of calcium dissolved in sea water, are discussed. Experiments were made at Lüttich, extending over one year; on the one side is an agricultural, and on the other, a manufacturing district. The mean of 266 analyses is 3·3526 volumes of carbonic anhydride per 10000 volumes of air; this high number is due to the local industries and to the slow oxidation of gases evolved from coal deposits under the whole district. As carbonic anhydride absorbs radiant heat more readily than air, an explanation is given of the high temperature of the district. Fall of snow or mist is accompanied with an increased amount of carbonic anhydride, it is greater in winter than in summer and with thunderstorms, but neither ordinary rain nor day nor night seem to have any marked effect. The amount of carbonic anhydride varies according to the direction of the wind, that is with the districts it passes over; the amount, moreover, decreases with high wind and increases with a high barometer. H. B.

Potassium and Sodium Selenides. By C. Fabre (*Compt. rend.*, **102**, 613—616).—*Sodium Selenides.*—The hydrate, $Na_2Se+16H_2O$, is obtained in needles by passing a rapid current of hydrogen selenide into a solution of 1 part of sodium hydroxide in 4 parts of water. The crystals melt in their water of crystallisation at 40°, and yield a colourless solution. When exposed to the air, they are converted into sodium carbonate and reduced selenium, with a small quantity of sodium selenite. The hydrate, Na_2Se+9H_2O, forms colourless crystals, and is obtained by the action of hydrogen selenide on a more concentrated solution of sodium hydroxide (3 parts in 1 of water) at a low temperature. The hydrate, $2Na_2Se+9H_2O$, is obtained in slender, white needles by the action of hydrogen selenide on a highly concentrated solution of sodium hydroxide, or better by adding an excess of the solid hydroxide to a solution of one of the preceding hydrates. The anhydrous selenide, Na_2Se, is obtained with some difficulty, owing to its corrosive action on glass. It is best prepared by heating the last hydrate in a current of nitrogen at a temperature not exceeding 400°. When fused, it has a reddish-brown colour, but when cold it forms a very hard, white, deliquescent, crystalline mass, which contains silicates and aluminates derived from the glass.

Potassium selenides are obtained by similar methods, but are much less stable. The hydrate, $K_2Se+19H_2O$, forms colourless crystals, and is obtained by the action of hydrogen selenide on a solution of 1 part of potash in 5 parts of water. The hydrate, $K_2Se+14H_2O$, is obtained by using a solution of 1 part of potash in 3 parts of water; it forms long, flexible needles. The hydrate, K_2Se+9H_2O, forms colourless, slender needles, which are extremely unstable when exposed to the air. It is obtained by the action of hydrogen selenide on a highly concentrated solution of potash. The anhydrous compound can only be obtained with very great difficulty, since it attacks glass in the same manner as the sodium compound. C. H. B.

Variations in the Solubility of Chlorides in Presence of Hydrochloric Acid. By R. Engel (*Compt. rend.*, **102**, 619—621).—Experiments with barium, sodium, ammonium, and strontium

chlorides lead to the conclusion that the solubility of chlorides which are precipitated from their aqueous solutions by hydrochloric acid, diminishes in presence of this acid by a quantity which corresponds with one equivalent of chloride for each equivalent of hydrochloric acid added, or, in other words, the sum of the equivalents of the chloride and the acid remains practically constant. In all cases, except that of ammonium chloride, in which the sum of the equivalents increases slightly but continuously, the sum of the equivalents at first diminishes slightly and then increases. When the solubility of the chloride has been diminished to less than one-fourth of its solubility in water, the law no longer holds good. C. H. B.

Calcium Hydroxide as a Boiler Incrustation. By O. Luedecke (*Zeit. Kryst. Min.*, **11**, 255—256).—The author has recorded the occurrence of brucite as a boiler incrustation. An analogous occurrence of calcium hydroxide has been recently brought under his notice. From the ice factory of Vaas and Littman, he received an incrustation deposited in the Carré ice machine. A quantitative analysis gave the following results:—

CaH_2O_2.	$CaCO_3$.	$Fe_2H_6O_6$.	Total.
94·77	1·95	3·75	100·47

The substance thus consists for the most part of calcium hydroxide. It occurs as tabular grey crusts, consisting of white lamellæ of the tetragonal system. B. H. B.

Atomic Weight of Beryllium. By S. T. Humpidge (*Proc. Roy. Soc.*, **39**, 1—19).—Determinations of the specific heat of beryllium made at various temperatures up to 447°, show that it rapidly increases up to about 400°, and that between 400° and 500° it remains practically constant at the approximate value of 0·62. This, if multiplied by the atomic weight taken as 9·1, gives 5·64 as the atomic heat. It seems, therefore, that the atomic weight, 13·6, previously deduced from the specific heat between 10° and 100° is incorrect, that beryllium must be classed with those elements of which the specific heat increases rapidly with the temperature, and that like most metals with low atomic weights, its atomic heat is considerably below the average.

Determinations were also made of the vapour-densities of beryllium chloride and bromide in V. Meyer's apparatus, but as the chloride attacks glass and porcelain, a platinum vessel was employed. The chloride has the density 2·733 at 635° and 2·714 at 785°; the bromide gives 6·336 at 606—630° (mean of three determinations). These results confirm those obtained for the chloride by Nilson and Pettersson (Abstr., 1884, 820), and show that these salts must have the formula $BeCl_2$ and $BeBr_2$, the atomic weight of beryllium being 9·1.

A. J. G.

The Earth Yα. By W. Crookes (*Compt. rend.*, **102**, 646—647).—An earth which becomes concentrated in the middle fractions of the earths from samarskite, gives a well-marked phosphorescence

spectrum. A sample of this earth was found to have the same chemical properties and to give exactly the same phosphorescence spectrum as a sample of the earth $Y\alpha$ prepared by Marignac.

A specimen of mosandrium prepared by Lawrence Smith gave a phosphoresence spectrum which shows that it is a mixture of which yttrium is one of the constituents. C. H. B.

Mosandrium. By L. de Boisbaudran (*Comp. rend.*, **102**, 647—648).—A sample of impure mosandria from Lawrence Smith's laboratory was carefully fractionated. After removal of didymium and samarium, the product had a deep orange-yellow colour, and gave the fluorescence spectra of $Z\beta$ and $Z\alpha$, especially the former. It also gave very distinctly the spectrum of $Y\alpha$, and hence mosandria is probably a mixture of $Y\alpha$ with terbia as Marignac has supposed. C. H. B.

Equivalent of Terbia. By L. de Boisbaudran (*Compt. rend.*, **102**, 483).—A correction concerning the proportion of holmium present in the samples of terbia described in a previous paper (this vol., p. 424). C. H. B.

Peroxides as Oxidising Agents. (By Pollacci (*Arch. Pharm.*, [3], **24**, 176).—Peroxides are usually employed as oxidising agents with the aid of acids, or at an elevated temperature. The author finds that lead and manganese peroxides more especially, exert a powerful action without these aids. The action is sufficiently powerful to set free iodine from metallic iodides, and to oxidise the nitrogen of organic and ammonium compounds to nitrous and nitric acids. By adding lead peroxide to potassium iodide solution, a yellow colour and alkaline reaction are immediately produced, and by the aid of starch solution iodine can be detected in solutions of its salts containing only 1 in 90000. Manganese peroxide acts similarly but more slowly; by passing carbonic anhydride, however, the action is much accelerated. If the peroxide be made into a paste with aqueous ammonia and placed in well-stoppered flasks for some time, hours in the case of lead peroxide and months in the case of manganese peroxide, almost all the ammonia becomes converted into nitrate and nitrite.

Broth and egg albumin also give rise to the formation of nitrate and nitrite, in contact with these peroxides. The amount of oxidisable matter may be quantitatively determined from the weight of lead oxide produced. J. T.

Formation and Dissociation of Barium and Strontium Manganites. By G. Rousseau (*Compt. rend.*, **102**, 615—618; see also this vol., p. 425).—The author has previously found that the dimanganite, $SrO,2MnO_2$, formed at a comparatively low temperature, is converted into the manganite SrO,MnO_2 at 1000—1100°. If this manganite is heated to bright redness (about 1600°) it is completely converted into the manganate. The barium compound behaves in a precisely similar manner, but the transformations take place at somewhat lower temperatures, the manganite being converted into the manganate at about 1500°.

The decomposition of the manganates of the alkaline earths seems to take place in a cycle. In the Bunsen flame, a manganite, RO,MnO_2, is formed, and at temperatures between the melting points of silver and copper this is converted into a dimanganite, $RO,2MnO_2$, which in its turn is reconverted into the manganite between the melting points of copper and gold. Lastly, the manganite is converted into the manganate at a temperature of about 1500—1600°.

As a matter of fact the composition of the product at any temperature is a result of equilibrium between the dissociating effect of the temperature and the oxidising action of the air. Both these effects may be rendered more evident by fusing the substance in a closed crucible or in a current of air, as the case may be.

The tension of dissociation of the manganite increases regularly with the temperature, but the heat of formation of the manganate increases still more rapidly as the temperature rises, until at a bright red heat the manganite is completely converted into manganate.

C. H. B.

Two New Nickel Arsenates. By Coloriano (*Bull. Soc. Chim.*, **45**, 240—244).—A solution of 1 gram of nickel nitrate in 5 c.c. of water was precipitated by means of a solution of 0·5 gram of trisodium arsenate in 5 c.c. water, 35 c.c. water added to the mixture, and the whole heated for six hours in closed tubes at 235—260°. The liquid was then found to contain crystals, together with unchanged amorphous nickel arsenate. The crystals were separated from the amorphous precipitate by levigation. The presence of an excess of nickel nitrate appears to be necessary for the formation of the crystals, or at all events facilitates it. No crystals could be obtained when nickel sulphate was substituted for the nitrate. The crystals had the formula Ni_2HAsO_5, but did not begin to give up water below the temperature of boiling sulphur, and were not completely dehydrated below a red heat. The author concludes, therefore, that the water is not water of crystallisation, and ascribes to the salt the constitution $Ni:AsO_4{\cdot}Ni{\cdot}OH$, corresponding with that of the mineral olivenite, $Cu:AsO_4{\cdot}Cu{\cdot}OH$, which was obtained artificially from copper arsenate by Friedel and Sarasin in manner similar to the above. This nickel arsenate forms transparent, green, hexagonal prisms, which are only attacked with difficulty by potash, mineral acids, or even aqua regia, but readily if heated with dilute hydrochloric acid in closed tubes at 180°. The same salt was obtained when an excess of nickel carbonate was digested with arsenic acid, and the mixture (diluted with water) heated in closed tubes at 240—265°. In this case, however, a second salt was also formed, which has the constitution $Ni(AsO_4H{\cdot}NiOH)_2$. This salt crystallises in deeper green hexagonal scales, which are rather less resistant to the action of acids and potash. It only begins to give up its water at about 350°, and is not completely dehydrated below a red heat.

L. T. T.

Isomeric Modifications of Chromic Chloride. By A. Recoura (*Compt. rend.*, **102**, 515—518, and 548—551).—If a saturated solution of green chromic chloride prepared by any method is treated

with a current of hydrogen chloride, half the dissolved salt is precipitated in the form of emerald-green crystals, which, when dried on porous plates, have the composition $Cr_2Cl_6 + 13H_2O$. 130 parts of the crystals dissolve in 100 parts of water, with practically no thermal disturbance. The solution has at first an emerald-green colour, and its absorption-spectrum shows a single green band, which is practically coextensive with the green of the spectrum. If the solution is allowed to remain it becomes darker in colour, and after about ten days changes to a blue-violet. The spectrum then shows a more or less intense red band as well as the green band.

If the green solution is precipitated by an equivalent quantity of sodium hydroxide, and the precipitate is *immediately* redissolved in an equivalent quantity of hydrochloric acid, a violet solution is obtained. The thermal disturbances corresponding with these changes were measured.

(1.)	Cr_2Cl_6, green, diss. + $3Na_2O$ diss. = 6NaCl diss. + Cr_2O_3 pptd.	develops + 63·0 cal.
(2.)	Cr_2O_3 pptd. + 6HCl diss. = Cr_2Cl_6, blue, diss.	„ + 41·4 „
(3.)	Cr_2Cl_6, blue, diss. + $3Na_2O$ diss. = 6NaCl diss. + Cr_2O_3 pptd.....	„ + 44·4 „
(4.)	Cr_2O_3 pptd. + 6HCl diss. = Cr_2Cl_6, blue, diss.	„ + 40·8 „

When correction is made for the heat of formation of the sodium chloride, these results show that the heat developed by the conversion of the green chloride into the blue chloride is 18·8 cal. The successive action of sodium hydroxide and hydrochloric acid on a solution of the green chloride which had changed spontaneously into the blue modification, gave the same results as experiments (3) and (4).

The blue-violet modification can be isolated in the same way as the green variety, by saturating a solution with hydrogen chloride. A concentrated solution of the blue-violet chloride is readily obtained by heating a solution of the green variety, but if this solution is too strong, conversion does not readily take place; a solution of 1 part of the salt in 1 part of water is a convenient strength. The precipitated chloride is dried on porous tiles. It forms a grey powder, which has the same composition as the green variety, $Cr_2Cl_6 + 13H_2O$, and is very soluble in water, yielding a blue-violet solution, identical in its properties with the solution formed by the alteration of the green chloride. Unlike the green variety, however, its solution is accompanied by a very considerable development of heat, + 24·04 cal., and hence whereas the conversion of the green solution into the blue-violet solution corresponds with a development of 18·8 cal., the conversion of the solid green chloride into the solid grey chloride corresponds with an absorption of 5·32 cal. From this result, it follows that the blue-violet form is the stable form in moderately dilute solutions, whilst in the solid state or in highly concentrated solutions the green variety is the more stable.

Anhydrous chromic chloride, when dissolved in water containing a

trace of chromous chloride, forms a green solution, from which the green chloride can be separated. The heat developed when this solution is precipitated with soda, is only + 52·4 cal., instead of + 63·0, and this result is independent of the dilution of the solution. The difference is probably connected with the function of the chromous chloride.

The solutions of chromic chlorides obtained by the ordinary methods are mixtures of the green and blue-violet varieties. Whatever the condition of the chromic chloride, the chromic hydroxide precipitated by addition of an equivalent quantity of potassium hydroxide is always the same. C. H. B.

Sulphur Compounds of Tungsten. By E. Corleis (*Annalen*, **232**, 244—270).—*Potassium monothiotungstate*, $K_2WO_3S + H_2O$, is prepared by passing hydrogen sulphide into a concentrated solution of potassium tungstate, until a slight yellow precipitate is formed. The colourless, deliquescent crystals are deposited when the filtered solution is mixed with five times its volume of alcohol. With an aqueous solution of the salt, zinc sulphate gives a white precipitate soluble in hydrochloric acid. When hydrogen sulphide is passed into a strong ammoniacal solution of ammonium tungstate, yellow prismatic crystals of *ammonium dithiotungstate*, $(NH_4)_2WO_2S_2$, are deposited. The crystals are triclinic, $a : b : c = 0·703 : 1 : 0·3392$. The salt is stable when dry, but decomposes easily in the moist state.

Potassium trithiotungstate, $K_2WOS_3 + H_2O$, is obtained in quadratic plates by the prolonged action of hydrogen sulphide on potassium tungstate. It dissolves freely in water, deliquesces in a damp atmosphere, and effloresces in a dry atmosphere. The solution gives a lemon-coloured precipitate with zinc sulphate.

Normal ammonium thiotungstate, $(NH_4)_2WS_4$, is prepared by the prolonged action of hydrogen sulphide on a dilute solution of ammonium tungstate. This salt crystallises in rhombic prisms or plates ($a : b : c = 0·7783 : 1 : 0·5673$) of an orange colour. It is isomorphous with ammonium thiomolybdate. It dissolves freely in water and in ammonia. In the moist state, it is unstable, and it is converted into tungsten bisulphide by ignition in an atmosphere of carbonic anhydride; it is slowly reduced to the metallic state by ignition in hydrogen.

Tungsten trisulphide is obtained in the pure state as a chocolate powder by adding hydrochloric acid to a solution of ammonium thiotungstate in an apparatus from which the atmospheric air has been expelled. The sulphide dissolves in solutions of alkaline carbonates, expelling carbonic acid.

Commercial tungstic acid frequently contains traces of molybdic acid. One of the two ammonium thiotungstates described by Berzelius really consists of a mixture of ammonium thiotungstate with a small quantity of the isomorphous thiomolybdate.

Normal potassium thiotungstate, K_2WS_4, is precipitated on the addition of potassium hydrogen sulphide and alcohol to a solution of ammonium thiotungstate. The potassium salt crystallises in rhombic prisms [$a : b : c = 0·7495 : 1 : 0·5665$]. It is freely soluble in water. The *sodium* salt, prepared by a similar reaction, is exceedingly

soluble in water, and is very hygroscopic. These salts do not form a precipitate with zinc sulphate.

The sulphur in these compounds was estimated by means of a standard solution of iodine. The alkali and tungsten were determined by precipitating the tungsten with freshly prepared mercurous nitrate, and weighing the tungsten as the trioxide. After removing the mercury from the filtrate, the alkali was converted into sulphate and weighed. W. C. W.

Complex Inorganic Acids. By W. Gibbs (*Amer. Chem. J.*, **7**, 392—417; compare this vol., p. 426).—*Antimonoso-phospho-tungstates.*—Only one salt is described; it cannot be recrystallised. The analysis leads to the formula $5Sb_2O_3,6P_2O_5,22WO_3,12K_2O + 48H_2O$.

Antimonio-tungstates.—These salts have already been mentioned as being formed by oxidation of the antimonoso-tungstates.

The salt $4Sb_2O_5,12WO_3,6K_2O + 25H_2O$ forms colourless, granular crystals.

Antimonio-molybdates.—$4Sb_2O_5,7MoO_3,5(NH_4)_2O + 12H_2O$, forms beautiful, colourless crystals.

Pyrophospho-tungstates are formed generally by boiling tungstic hydrate with an alkaline pyrophosphate: the phosphoric acid can only be separated by the ordinary reagents after boiling several times with hydrochloric acid. $6(NH_4)_4P_2O_7,3Na_4P_2O_7,2(NH_4)_2O,22WO_3 + 31H_2O$, forms a white, crystalline precipitate. $9K_4P_2O_7,22WO_3 + 49H_2O$ is a white, granular precipitate. $6K_4P_2O_7,3H_4P_2O_7,K_2O,H_2O,22WO_3 + 42H_2O$ is a white, crystalline salt. This series corresponds in a measure with Wallroth's pyrophosphates containing $9(P_2O_5)$.

Monometaphosphotungstates are obtained by the direct action of glacial phosphoric acid on the acid tungstates. $2KPO_3,3K_2O,24WO_3 + 20H_2O$ is a soft crystalline mass; from the mother-liquor another salt was obtained, but not completely analysed.

The salt $2NH_4PO_3,(NH_4)_2O,18WO_3 + 11H_2O$ is a white, crystalline mass.

Orthometaphosphotungstates.—One salt was prepared by boiling sodium phosphotungstate (1 : 24) with sodium monometaphosphate, and adding potassium bromide. It is a white, gelatinous mass, contains phosphoric acid in two modifications, and is expressed by the formula $6P_2O_5,11K_2O,7Na_2O,22WO_3 + 42H_2O$.

Monometaphosphomolybdates.—In this class there are two series of salts, the one crystalline, the other gummy.

The salt $4NH_4PO_3,3(NH_4)_2O,10MoO_3 + 9H_2O$ forms colourless, flat crystals, that may be recrystallised from water.

Hexametaphospho-molybdates.—The barium salt,

$$3P_2O_5,4BaO,14MoO_3 + 55H_2O,$$

forms acicular crystals.

Stanno-phospho-tungstates.—Only the ammonium salt is fully described; it is a white, crystalline precipitate of the formula

$$2SnO_2,P_2O_5,2(NH_4)_2O,22WO_3 + 15H_2O.$$

Stanno-phospho-molybdates are formed like the preceding salts.

$4SnO_2,3P_2O_5,3(NH_4)_2O,16MoO_3 + 28H_2O$ is a bright yellow crystalline precipitate.

Reference is made to H. Struve and Parmentier's alumino-, ferrico-, and chromico-molybdates; the first series at any rate corresponds with Klein's borotungstates, and the last two series, and others also, will probably be found to correspond.

A list of salts so far described is given, in which the following are marked as being less certainly established:—$7As_2O_5,6V_2O_5,3H_2O$; $4V_2O_5,VO_2,5P_2O_5,4Na_2O + 37H_2O$; $5As_2O_3,(NH_4)_2O,12MoO_3 + 24H_2O$; $As_2O_3,4As_2O_5,10K_2O,21WO_3 + 26H_2O$; $2KPO_3,5Na_2O,16WO_3 + 20H_2O$; $(Ba_36PO_3),BaO,14MoO_3 + 55H_2O$; $P_2O_5,V_2O_5,3K_2O,7WO_3 + 11H_2O$. H. B.

Antimony Sulphide. By Berthelot (*Compt. rend.*, **102**, 22—27).—An abstract of the greater part of this paper has already appeared (this vol., p. 308).

The formation of a chlorosulphide is indicated by the variations in the amount of heat developed by the action of hydrogen sulphide on solutions of antimony chloride of different strengths. When a solution containing $12{\cdot}44HCl + 240H_2O + SbCl_3$ is mixed with the exact quantity of hydrogen sulphide required for complete precipitation, the proportion of antimony chloride precipitated with the sulphide is somewhat less than a quarter of an equivalent.

If a solution of an antimony compound is added in very small drops with continual agitation to a saturated solution of hydrogen sulphide, the precipitate which forms is redissolved. This fact points to the formation of a hydrosulphide, which however can only exist in contact with water in presence of a large excess of hydrogen sulphide.

The somewhat considerable development of heat which takes place when antimony chloride is dissolved in concentrated hydrochloric acid indicates the existence of a hydrochloride. Fused antimony chloride absorbs 8 to 10 vols., or one-twentieth of an equivalent, of hydrogen chloride, which is not given off when the substance cools. If the compound is heated, the greater part of the hydrogen chloride is liberated, but is reabsorbed on cooling. Hydrochloric acid of the composition $HCl + 3{\cdot}73H_2O$ will dissolve more than five times its weight of antimony chloride, and if this solution is cooled to some degrees below 0° it solidifies to a seemingly homogeneous, crystalline mass, which melts again at the ordinary temperature. The hydrochloride of antimony chloride corresponds with the antimony potassium and antimony sodium chlorides described by Liebig and by Jacquelain.

Attempts were made to measure the heat of formation of sodium sulphantimonite by adding a solution of sodium sulphide to a solution of antimony chloride, but concordant values could not be obtained. Better results were obtained by adding hydrochloric acid to a dilute solution of the sulphantimonite; Sb_2S_3 pptd. $+ 3Na_2S$, dil $= 2Na_3SbS_3$, diss. develops + 22·4 cal. This value varies, however, with the degree of dilution. When sodium sulphide is added to antimony chloride, the solution contains principally a monosodium sulphantimonite analogous to the sulphantimonites which are found as minerals.

C. H. B.

Antimony and Bismuth Sulphates. By C. Hensgen (*Rec. Trav. Chim.*, **4**, 401—413).—Anhydrous antimony sulphate, $Sb_2(SO_4)_3$, is best prepared by dissolving the trisulphide in concentrated sulphuric acid heated to the temperature at which it commences to vaporise; the salt is deposited as a fine, very deliquescent, white, crystalline powder. Its products of decomposition with water vary with the conditions, such as mass and temperature; with boiling water, the salt is completely decomposed into antimonious oxide (containing less than 1 per cent. of water) and sulphuric acid, whilst with water at ordinary temperatures a basic sulphate, $5Sb_2O_3,2SO_3,7H_2O$, is produced. The sulphate is almost completely converted into antimonious chloride by a current of hydrogen chloride.

Anhydrous bismuth sulphate, $Bi_2(SO_4)_3$, prepared in a manner similar to the antimony salt, crystallises in very hygroscopic, glistening needles; when evaporated with water, it yields a slightly coherent powder of the composition $Bi_2(SO_4)_3 + 3H_2O$, but on treating it with water at the ordinary temperature and evaporating the solution, a powder of the composition $2Bi_2(SO_4)_3 + 7H_2O$ is obtained; lastly, if the salt be frequently treated with water, the final product is a hydrate, Bi_2O_3,SO_3,H_2O. It is probable that under favourable conditions the sulphate is converted by hydrochloric acid into bismuth trichloride.

V. H. V.

Mineralogical Chemistry.

Mineralogical Notes. By J. Loczka (*Zeit. Kryst. Min.*, **11**, 261—262).—1. *Gold from Vöröspatak.* Two analyses are given—

	Au.	Ag.	Quartz.	Total.	Sp. gr.
I.	72·49	27·60	—	100·09	16·0022
II.	66·38	33·22	0·42	100·02	15·0080

I. Gold in leaves; II. Aggregate of small icositetrahedra.

2. *Garnet from Csiklova.*—Sp. gr. 3·6103. Analysis gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
39·65	18·85	5·36	0·21	35·65	0·82	0·11	0·08	0·56	101·29

corresponding with the formula $(Ca,Mg)_3(Al,Fe)_2(SiO_4)_3$.

3. *Löllingite from St. Andreasberg.*—Sp. gr. 7·4746. Analysis gave—

S.	As.	Sb.	Cu.	Fe.	SiO_2.	Total.
0·84	68·08	4·03	0·10	27·32	0·10	100·47

Formula $Fe(As,Sb)_2$.

4. *Augite from Dognácska.*—Sp. gr. 3·5573. Analysis gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	Total.
48·38	0·68	3·23	15·88	7·94	22·10	2·22	0·10	0·18	100·71

All the above minerals were from the collection of the Hungarian National Museum. B. H. B.

Minerals from Bolivia. By A. Arzruni (*Jahrb. f. Min.*, 1886, 1, Ref. 198—199).—The minerals described are: *tinstone* from Oruro, *native bismuth* from the Cariviri and Jucamariri mines at Sarasora, *arsenical pyrites* occurring in a sericitic limestone, remarkable for the step-like development of the crystals, and *edible earth*, the *pasa* of the natives. The last-named substance consists of magnesia, silica, alumina, ferric oxide, lime, water, and traces of soda; the greater portion consisting of magnesia. It is eaten not only by the natives, but also by the whites in enormous quantities (up to 5 grams daily). The author regards it as a decomposition-product of the granitic felspars and magnesia-mica. B. H. B.

Analyses of Hungarian Arsenical Pyrites. By J. Loczka (*Zeit. Kryst. Min.*, **11**, 268—270).—As hitherto the only Hungarian arsenical pyrites analysed is that from Oravicza, the author has analysed the arsenical pyrites from Felsöbánya (I), Zalathna (II), Rodna (III), the Bindt in Zips County (IV), and Csiklova (V), with the following results:—

	S.	Sb.	As.	Fe.	Co.	Au.	Residue.	Total.	Sp. gr.
I.	21·11	0·28	42·94	35·04	—	—	—	99·37	6·167
II.	20·59	0·14	43·37	35·30	—	0·07	0·42	99·89	6·122
III.	21·82	0·16	42·04	35·72	—	—	—	99·74	6·078
IV.	20·10	—	45·12	35·04	0·06	—	—	100·32	6·090
V.	20·24	trace	45·23	34·78	0·30	—	0·11	100·66	6·160

These analyses correspond with the formulæ: I and II, $Fe_{15}S_{16}As_{14}$; III, $Fe_9S_{10}As_8$; IV and V, FeAsS. The material employed was obtained from the collection of the Hungarian National Museum. B. H. B.

The Fahlerz of Przibram. By F. Babanek (*Zeit. Kryst. Min.*, **11**, 271—273).—The analyses gave the following results:—

	I.	II.	III.	IV.
Quartz.....	17·50	—	—	—
Sb	17·86	21·20	23·0	25·00
Zn	5·80	10·70	2·0	—
Fe	2·58	7·28	2·4	—
Pb	12·00	—	10·8	41·80
Cu	14·91	24·34	10·8	12·69
Ag	3·40	5·32	26·1	—
S	16·84	22·89	(24·9)	(20·51)
$CaCO_3$.....	4·80	—	—	—
CO_2 and O	2·70	8·30	—	—
Totals	98·39	100·03	100·0	100·00

I. Compact fahlerz from the Franzisci vein, formula

$$5(PbS,Cu_2S,Ag_2S) + 2Sb_2S;$$

II. Compact fahlerz from the Upper Schwarzgrube vein, formula $5(Ag_2S,Cu_2S) + 2Sb_2S_3$; III. Fahlerz in small crystals from the Fundgrube vein at the Anna mine, formula $2(Ag_2S)Sb_2S_3 + 4(Cu_2S,PbS,ZnS,FeS)Sb_2S_3$; IV. Compact dark-green mineral (bournonite) from the Franzisci vein, formula $2(Cu_2S)Sb_2S_3 + 4(PbS)Sb_2S_3$.

B. H. B.

Cosalite, Alaskaite, and Beegerite. By G. A. Koenig (*Zeit. Kryst. Min.*, **11**, 290—291).—The author has found cosalite (Analysis I) associated with alaskaite (Analysis II) in the Alaska Mine, Ouray Co., Colorado. The two minerals are so intimately associated that it is difficult to separate them. The author has also analysed a finely granular lead-grey mineral (III), which was rendered impure by pyrites, barytes, and quartz. Sp. gr. 6·565. It was found at the Old Lout Mine. The calculated formula is $6(PbAg_2)S + Bi_2S_3$, that of beegerite. The analytical results were as follows:—

	S.	Bi.	Pb.	Ag.	Cu.	Fe.	Zn.	Insol.	Total.
I.	17·13	43·54	26·77	1·35	8·78	0·52	trace	0·60	98·69
II.	17·98	53·39	12·02	7·80	5·11	0·84	0·34	1·80	99·28
III.	16·39	19·35	45·87	9·98	1·12	2·89	—	0·12	95·72

B. H. B.

Thiobismuthite of Lead and Silver. By E. Le Neve Foster (*Zeit. Kryst. Min.*, **11**, 286).—This mineral was found at the Loreto Mine in the Sierra Madre Mountains, Mexico. It is compact, whitish-grey, and has a metallic lustre. Sp. gr. 5·8, H. = 3 to 3·5. Analysis gave—

Bi.	S.	Pb.	Cu.	Ag.	Fe.	Zn.	SiO_2.	Ignition.	Total.
34·51	15·56	21·51	2·32	13·47	0·87	0·60	9·01	0·76	98·61

B. H. B.

The Bluish-grey Mineral Crusts from Rodna. By B. Medgyesy (*Zeit. Kryst. Min.*, **11**, 262).—The author shows that the bluish-grey crusts found in 1880 on the crystalline masses of pyrites and galena at Rodna (*Zeit. Kryst. Min.*, **8**, 538) consist of a mixture of several minerals. B. H. B.

Blue Rock Salt. By C. Ochsenius (*Jahrb. f. Min.*, 1886, **1**, Mem., 177).—In 1877, the author stated that the blue colour of certain varieties of rock salt from the Stassfurt deposit was probably due to sulphur. O. Precht (Abstr., 1883, 1051) came to the conclusion that the blue colour was due to optical phenomena. This result induced the author to investigate the optical properties of a dark-blue specimen from the Douglashall shaft. He found that by placing the sodium line at 50 on the Steinheil scale, the middle of a symmetrical absorption-band, about 10 divisions wide, appeared at 39; whilst in the aqueous solution of the mineral no absorption-band could be detected. These results confirm Precht's theory. B. H. B.

Crystallographic Study of the Thinolite of Lake Lahontan. By E. S. Dana (*Zeit. Kryst. Min.*, **11**, 285—286).—The characteristic feature of the Lahontan basin, N.W. Nevada, is the great abundance

of calcareous tufas. The tufa is of great economical interest, and is termed by the author thinolite (from θὶς, shore). Analysis gave—

CaO.	MgO.	$Fe_2O_3 + Al_2O_3$.	CO_2.	H_2O.	Insol.	Total.
50·45	1·37	0·71	40·90	1·50	3·88	98·81

with traces of P_2O_5, Cl, and SO_3.

The examination of sections showed that the structure of thinolite is crystalline, and the crystals present an open skeleton appearance. The original mineral may have been a calcium chlorocarbonate isomorphous with phosgenite. In conclusion, the author discusses the relation of thinolite to the so-called gaylussite pseudomorphs of Sangerhausen and other localities, and concludes that the original mineral deposited on an enormous scale in the Lahontan basin was most probably the same as that which formed the well-known Sangerhausen pseudomorphs. B. H. B.

Discovery of Turquoise (Calaite) in Russia. By N. v. Kokscharoff (*Jahrb. f. Min.*, 1886, **1**, Ref., 10).—The mineral which has a slightly green colour, and is insoluble in hydrochloric and nitric acids, was found with wollastonite in the copper mines of Karalinsk, in the Kirghiz Steppes. Analysis gave—

Al_2O_3.	Fe_2O_3.	CuO.	P_2O_5.	Ignition.	Total.
35·79	3·52	7·67	34·42	18·60	100·00

A mineral found in the Syrjanowsk mine (Altai) and described as turquoise has since proved to be alumstone. B. H. B.

Epsomite from the Peychagnard Anthracite Mine. By Kuss (*Jahrb. f. Min.*, 1886, **1**, Ref., 192).—In an old adit level of the Peychagnard Anthracite Mine, Isère, a layer of bitter salt 10 to 15 cm. thick has been found. In this crystals 6 cm. in length occur. The sulphuric acid from the iron pyrites in the anthracite has acted on the dolomitic rock, forming bitter salt, which is here found for the first time in large natural crystals. B. H. B.

Rare Minerals from Utah. By W. F. Hillebrand (*Zeit. Kryst. Min.*, **11**, 286—288).—The minerals analysed are from the American Eagle Mine, Tintic mining district, Utah, several being new to America.

1. *Olivenite* (wood copper), formula $Cu_3As_2O_8 + H_2CuO_2$.

As_2O_5.	P_2O_5.	CuO.	H_2O.	Fe_2O_3.	CaO.	SiO_2.	Total.
40·05	0·06	55·40	3·39	0·25	0·16	0·40	99·71

2. *Konichalcite*, formula $(Cu,Ca)_3As_2O_8 + H_2CuO_2 + \frac{1}{2}H_2O$.

As_2O_5.	P_2O_5.	CuO.	CaO.	MgO.	ZnO.	H_2O.	Ag.
39·94	0·14	28·68	19·79	0·54	2·86	5·52	0·30

Fe_2O_3.	CO_2.	SiO_2.	Total.
0·36	(0·97)	0·90	100·00

3. *Chenevixite;* compact, colour olive-green, opaque, H. 3·5, fracture semi-conchoidal.

As_2O_5.	CuO.	CaO.	MgO.	Fe_2O_3.	Al_2O_3.	H_2O.	SiO_2.	Total.
35·14	26·31	0·44	0·16	27·37	0·66	9·33	0·40	99·81

4. *Jarosite* is found with the above-mentioned minerals in the form of slender, brown, transparent crystals. B. H. B.

Pharmacosiderite and Urvölgyite from a New Locality. By J. v. Szabó (*Zeit. Kryst. Min.*, **11**, 266—267).—The author has found pharmacosiderite and urvölgyite (herrengrundite) in the abandoned copper mines of the Sandberg, between Altgebirg and Herrengrund in Hungary. B. H. B.

Synthetical Studies. By C. Doelter (*Jahrb. f. Min.*, 1886, **1**, Mem., 119—135).—1. *Artificial calcium silicate*, $CaSiO_3$.—The author has repeated the experiments of Bourgeois (Abstr., 1884, 564) to reproduce wollastonite artificially, and carefully studied the calcium silicate formed at a high temperature. In the first place, natural wollastonite from Auerbach was fused, and cooled slowly. After a few hours, a coarsely crystalline mass was obtained, which differed crystallographically from natural wollastonite. The sp. gr. was 2·88. The crystals obtained by fusing equivalent amounts of CaO and SiO_2, appear to be hexagonal, thus indicating that calcium silicate is dimorphous. It is, however, not impossible that the crystals are rhombic. The sp. gr. of this artificial calcium silicate is 2·905. In order to obtain products corresponding with wollastonite, a high temperature must be avoided. Gorgeu (Abstr., 1884, 1262) obtained wollastonite by fusing silica with calcium chloride at a cherry-red heat in a current of moist air. The crystals obtained (sp. gr. 2·88, H. 3·5) were biaxial, but do not appear to have corresponded with the tabular form of wollastonite crystals. The opinions of Bourgeois and Gorgeu are exactly opposed with reference to calcium silicate produced at a low temperature (dark red heat). The author has therefore made a series of experiments and finds that in all cases in which steam is absent, a hexagonal product is obtained. This is also obtained at a high temperature. Natural wollastonite can thus only have been formed at a low temperature in the presence of steam.

2. *Pectolite and the silicate* $CaNa_2Si_2O_6$.—The silicate $CaNa_2Si_2O_6$ is usually included under the head of pectolite, and is frequently regarded as being isomorphous with wollastonite. Optically, however, the two minerals are entirely different. From the author's experiments, it is evident that the silicate $CaNa_2Si_2O_6$ behaves likes augite, whilst pectolite on fusion behaves like $CaSiO_3$. It is thus improbable that pectolite consisted originally of $CaNa_2Si_2O_6$. This view is confirmed by the fact that unaltered pectolite, like that from Bergenhill, always contains water.

3. *Experiments to imitate contact actions.*—The minerals occurring at the contact of eruptive rocks and limestone may be divided into four groups according to their mode of formation. 1. Augite, fassaite,

anorthite, labradorite, olivine, meionite, gehlenite, spinel, magnetite. 2. Garnet, hornblende. 3. Idocrase, humite, mica, wollastonite. 4. Serpentine, zeolite, brucite. The results of the author's experiments lead to the hypothesis that, at certain places, where only minerals of the first group occur as contact minerals, the action of the molten magma on limestone in the presence of carbonic anhydride, suffices as explanation of their formation. Where minerals of the second group occur so high a temperature need not have prevailed. Lastly, for many points of contact, where hydrated minerals like idocrase and mica present themselves as contemporaneous formations, the direct action of a molten magma should not be assumed.

B. H. B.

Orthoclase in Geodes in Basalt. By V. v. Zepharovich (*Jahrb. f. Min.*, 1886, **1**, Ref., 211—212).—In the cavities in the basalt (leucite-tephrite) of the Eulenberg, near Leitmeritz, the following series of minerals have been observed:—1. (oldest) Phillipsite; 2. Calcite; 3. Orthoclase (adularia); 4. Very small cubes of iron pyrites; 5. Calcite. An analysis of the orthoclase (sp. gr. 2·568) gave the following results:—Loss at 100°, 0·228; on ignition 0·452 more; total 0·680. The ignited substance gave—

SiO_2.	Al_2O_3.	K_2O.	Na_2O.	CaO.	Total.
63·64	19·46	15·00	1·84	0·16	100·10

B. H. B.

Microcline and Muscovite from Forst in the Tyrol. By K. Oebbeke (*Zeit. Kryst. Min.*, **11**, 256—257).—At Forst, near Meran, a coarsely granular granite rock (pegmatite) occurs in the gneiss. It consists of felspar, quartz, and silver-white mica, with black tourmaline and reddish-brown garnet as accessory minerals. Analyses are given of two specimens of the greyish-blue felspar (I and II), and of the muscovite (III):—

	SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.
I.	65·12	19·56	0·16	0·26	0·09	12·96	2·16
II.	65·04	19·23	0·16	0·22	0·09	13·25	1·74
III.	45·28	37·59	1·18	0·09	0·17	10·32	1·20

	H_2O.	Total.	Sp. gr.
I.	0·32	100·63	2·570
II.	0·36	100·09	2·577
III.	4·12	99·95	2·930

B. H. B.

Zygadite. By J. A. Krenner (*Zeit. Kryst. Min.*, **11**, 259—261).—This rare mineral described by Breithaupt in 1846, occurs in druses in the slate of St. Andreasberg in association with quartz and sphalerite. It consists of thin, acute rhombic tablets, exhibiting the forms $\infty\breve{P}\infty$, 0P, and $\breve{P}\infty$. A chemical analysis of 0·4608 gram gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
68·81	19·41	trace	0·30	trace	11·05	0·41	trace	99·98

From this, the author concludes that zygadite is a variety of albite. Albites of similar form occur at Kongsberg and in Dauphiné.

B. H. B.

Zeolite from a Pyroxenic Rock of Brazil. By GORCEUX (*Jahrb. f. Min.*, 1886, **1**, Ref., 188—189).—The zeolite was found in an amygdaloïdal rock in the Abaété basin, Minas Geraës, Brazil. It is white, fuses easily, and is decomposed by nitric acid. Sp. gr. 2·15. Analyses gave the following results :—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
I.	47·5	20·6	1·1	7·6	3·1	4·4	0·8	15·0	100·1
II.	46·9	21·5	2·4	7·0	2·3	4·6	1·6	15·0	101·3

From these analyses, the author concludes that the zeolite is phillipsite.

B. H. B.

Analyses of Minerals from Greenland. By J. LORENZEN (*Zeit. Kryst. Min.*, **11**, 315—318).—1. *Willemite*, from Trapp in Tunugdliarfik.

SiO_2.	ZnO.	FeO,MnO.	Insol.	Total.	Sp. gr.
26·01	74·18	0·41	0·10	100·70	4·11

The following minerals are from Fiskernaesset.

2. *Saphirine;* H. = 7·5; sp. gr. 3·46; colour, blue :—

SiO_2.	Al_2O_3.	FeO.	MgO.	Ignition.	Total.
12·95	64·44	1·66	19·83	0·34	99·22

Formula: $5MgAl_2O_4 + Al_2O_3(SiO_2)_2$.

3. *Kornerupine;* sp. gr. 3·23, H. = 6·5.

SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	H_2O.	Total.
30·90	46·79	2·02	19·46	1·30	100·47

Formula: $MgAl_2SiO_6$.

5. *Edenite* (Hornblende). Colour green (sp. gr. 307) or greyish-yellow (sp. gr. 306).

SiO_2.	Al_2O_3.	Cr_2O_3.	FeO.	CaO.	MgO.	Ignition.	Total.
46·79	15·36	0·69	2·38	13·11	20·17	2·13	100·63

Formula: $5RSiO_3 + Al_2O_3$.

6. *Kupfferite;* sp. gr. 3·21.

SiO_2.	Al_2O_3.	FeO.	MgO.	Ignition.	Total.
55·04	3·35	5·71	33·98	1·78	99·86

Formula: $28MgSiO_3 + Al_2O_3$.

7. *Kærsutite;* colour black, streak brown, H. = 5·5, sp. gr. 3·04.

SiO_2.	SnO_2.	TiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	Total.
41·38	0·26	6·75	14·41	11·28	12·97	13·51	100·56

Formula: $5R^{IV}R^{II}O_3 + Al_2O_3$.

Analyses are also given of analcime, microcline, and natrolite.

B. H. B.

Prochlorite from the Columbia District. By G. P. Merrill (*Zeit. Kryst. Min.*, **11**, 293—294).—The mineral occurs as a compact aggregate of small scales of a dark green colour: H. = 1·5; sp. gr. 2·835; optically biaxial with small axial angle. Analysis gave—

SiO_2.	Al_2O_3.	MgO.	FeO.	Na_2O.	H_2O.	Total.*
25·45	7·88	15·04	24·98	0·67	14·43	88·45

The mineral was found in Foundry Run, 1½ mile north-west of the city of Washington. It is associated with hornblende, epidote, pyrites, tourmaline, and rutile. B. H. B.

Quartz-felsites and Augite-granites from the Cheviot District. By J. J. H. Teall (*Geol. Mag.*, **2**, 106—121; *Jahrb. f. Min.*, 1886, **1**, Ref., 254—255).—The rocks described by the author as quartz-felsite, occur as dykes in the porphyrites of the Cheviot district. The analysis of the rock from Shillmoor Farm gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	Loss.	Total.
67·9	15·7	3·0	1·4	1·5	1·5	5·6	3·7	100·3

In the felsitic ground-mass, hexagonal tablets of mica, felspar, and quartz grains are detected. Under the microscope, the ground-mass appears to be microcrystalline. B. H. B.

Meteoric Iron from West Virginia. By G. F. Kunz (*Amer. J. Sci.*, **13**, 145—148).—The iron was found at Jenny's Creek, in the upper end of Wayne Co., West Virginia. Three fragments were found, the total weight being about 27 lbs. The iron is octahedral, and made up of crystalline blocks of plessite and kamacite. Between these are thin flexible plates of schreibersite. The original weight of the piece lent to the author for description was 275 grams. The surface is altered to limonite to a depth of 2 mm. The Servier Co., Tennessee, and the Arva irons approach it most closely in structure. Analysis gave the following results:—

Fe.	P.	Ni + Co.	Total.	Sp. gr.
91·56	0·13	(8·31)	100·00	7·344

The iron does not exhibit any Widmannstätten figures, the crystalline structure being really brought out in relief by the schreibersite between the crystalline faces of the iron. B. H. B.

* 98·45 in the original.

Organic Chemistry.

Pyrrolylene. By G. Ciamician and P. Magnaghi (*Ber.*, **19**, 569—574; compare Abstr., 1885, 1242).—The tetrabromide obtained from pyrrolylene (*loc. cit.*) is shown by direct comparison to be identical with that from Henniger's butine (*Ber.*, **6**, 70). It forms colourless needles melting at 118—119°. The light petroleum mother-liquor obtained in purifying the above bromide from either source yielded a second *tetrabromide*, $C_4H_6Br_4$; this crystallises in large prismatic crystals, melting at 39—40°. The identity of the bromides (m. p. 39—40°) from pyrrolylene and from butine was further shown by crystallographic measurements.

There is not sufficient evidence to show whether the two bromides (m. p. 39—40° and 118—119°) are isomerides, or whether one or the other may not have the formula $C_4H_4Br_4$ instead of $C_4H_6Br_4$. Both compounds when heated at 120° with saturated alcoholic ammonia, yield a sparingly soluble white mass; the filtrate from this when freed from excess of ammonia, colours a chip of pine-wood moistened with hydrochloric acid intense red; a solution of isatin acidified with acetic acid acquires a green colour when treated with the alcoholic solution. This evidence is insufficient to decide whether pyrroline has been formed or not. N. H. M.

Action of Ammonia and Water on Chloroform. By G. André (*Compt. rend.*, **102**, 553—555).—When chloroform is heated with aqueous ammonia (4 mols.) in sealed tubes at 200—225° for six hours, it is completely decomposed. No cyanide is formed, and the products are carbonic oxide, ammonium chloride, and ammonium formate, the ratio of chloride to formate being 6 : 1. The decomposition is in all probability represented by the equation $2CHCl_3 + 7NH_3 + 3H_2O = CO + 6NH_4Cl + HCOONH_4$.

If the tubes are only heated to 180°, part of the chloroform remains undecomposed. These results confirm those obtained by Heintz.

If chloroform is heated in sealed tubes at 225° for five hours with 10 times its volume of water, it is decomposed into carbonic oxide, hydrochloric acid, and formic acid, the ratio between the two acids being 15 : 1. If the tube is opened at the end of five hours to allow the gas to escape, and is then heated to the same temperature for a further period of five hours, 75 per cent. of the chloroform is decomposed, and a much larger quantity of hydrochloric acid is formed, the ratio between this acid and the formic acid being 25 : 1.

If formic acid is heated with water under the same conditions it is decomposed into water and carbonic oxide, decomposition taking place more readily in presence of a small quantity of some other acid. This decomposition has already been studied by Berthelot and by Riban. C. H. B.

Synthesis of Hydrocyanic Acid. By A. Figuier (*J. Pharm.* [5], **13**, 314).—A mixture of one volume of methane with two volumes

of nitrogen was subjected to the silent electric discharge, when ammonium cyanide was formed. J. T.

The Ferrocyanides of Methylamine and Piperidine. By T. Hiortdahl (*Zeit. Kryst. Min.*, **11**, 251—254).—These compounds were prepared and examined crystallographically by the author in order to determine whether the ferrocyanides of the amines present any analogy to potassium ferrocyanide. Only two organic ferrocyanogen compounds could be obtained sufficiently well crystallised. The methylamine salt presents no analogy to potassium ferrocyanide; it contains no water of crystallisation. The piperidine salt, on the other hand, has a composition similar to that of potassium ferrocyanide, in that it contains 3 mols. H_2O. It crystallises in the triclinic system, but in forms closely resembling the monoclinic crystals of potassium ferrocyanide. The results of the author's measurements were as follows:—

1. Methylamine hydroferrocyanide, $(NH_2Me)_4,H_4Fe(CN)_6$, tetragonal; $a : c = 1 : 0{\cdot}7889$.

2. Piperidene hydroferrocyanide, $(C_5H_{10}{\cdot}NH)_4,H_4Fe(CN)_6 + 3H_2O$, triclinic; $a : b : c = 0{\cdot}6135 : 1 : 0{\cdot}6081$; $\alpha = 83°\ 53'$, $\beta = 90°\ 36'$, $\gamma = 88°\ 4'$. The axial ratio for potassium ferrocyanide is $a : b : c = 0{\cdot}5731 : 1 : 0{\cdot}5689$; $\beta = 89°\ 31'$. B. H. B.

Normal Melamines. By P. Klason (*J. pr. Chem.* [2], **33**, 290—300).—Samples of melamine prepared from crude melam, cyanuric chloride, or from substituted cyanamides, have similar crystallographic and optical properties, and are in fact identical. Melamine crystallises in short, tabular, monoclinic prisms, $a : b : c = 1{\cdot}4091 : 1 : 0{\cdot}9783$; $\beta = 68°\ 13'$. The crystals are tolerably transparent, and the double refraction is negative. The author confirms Hofmann's formula for the platinochloride.

Normal trimethylmelamine melts at about 115°, it distils slowly but without decomposition at 360°; it is best prepared by passing methylamine into a well-cooled ethereal solution of cyanuric chloride; by thus modifying Hofmann's process, the formation of bye-products is avoided.

Normal triethylmelamine may be prepared by passing ethylamine through a well-cooled ethereal solution of cyanuric chloride until it becomes alkaline, when diethylamine cyanochloride is formed. This is cooled, saturated with ethylamine, and then heated for several hours at a little above 100°; the solution is concentrated, treated with potash, and the triethylamine extracted with ether. It is very readily soluble in ether and alcohol, less so in hot water, from which it crystallises in needles; it melts at 73°; its salts are volatile, readily soluble and crystallise in needles; it forms a *platinochloride*, $C_9H_{18}N_6,H_2PtCl_6$, which on treatment with water is converted into the salt $(C_9H_{18}N_6)_2,H_2PtCl_6$.

Normal triphenylmelamine, prepared in a manner similar to the preceding compounds, is very sparingly soluble in the usual solvents, but dissolves with tolerable ease in boiling glacial acetic acid; it crystallises in slender needles, melts at 225°, and sublimes at 360°. When heated

with hydrogen chloride at 200°, it is decomposed into cyanuric acid and aniline; it seems not to have basic qualities.

Normal paratritolylmelamine, prepared in a manner similar to the preceding compounds from cyanuric chloride and paratoluidine, is an indifferent compound, insoluble in most of the usual solvents, but may be crystallised in needles from glacial acetic acid; it melts at 283°.

Starting from the chlorocyanuric diamines, a large number of melamines may be prepared; of these only monophenylmelamine is mentioned, it is prepared by heating chlorocyanuric diamine and aniline at 150°; it is tolerably soluble in alcohol, crystallises in prisms, and melts at 284°; it has basic properties. The *chloride* and *platinochloride*, $2C_3N_3NHPh(NH_2)_2,H_2PtCl_6$, were prepared.

The ammelide prepared by Liebig from melam consists of a mixture of ammeline and melanuric acid, ammelide in fact having no existence; the author therefore proposes to designate melanuric acid as ammelide for the future, as being a more suitable name. Ammeline may be prepared either by heating melam with dilute potash, hydrochloric acid, or concentrated sulphuric acid at 100°; or by treating chlorocyanuric diamide with alkalis, or by the oxidation of thioammeline with potassium permanganate; or by boiling the ethereal salts of either diamidocyanuric or diamidothiocyanuric acids with hydrochloric acid. Ammeline may be separated from ammelide (the melanuric acid of Liebig) by dissolving the mixture in warm soda and cooling, when the ammeline is precipitated almost completely whilst the ammelide remains in solution; *ammeline hydrochloride*, $HO(CN)_3(NH_2)_2,HCl$, dissolves very sparingly in water, and crystallises in small prisms.

Thioammeline may be prepared by dissolving chlorocyanuric diamide in a concentrated solution of potassium sulphide, and precipitating with acetic acid; one part of thioammeline dissolves in 310 parts of boiling water, from which it crystallises in slender needles; these when dry form a soft woolly mass. It is readily soluble in alkalis and mineral acids; its salts crystallise well. The *sulphate* forms large sparingly soluble prisms; the *hydrochloride*, $SH(CN)_3(NH_2)_2,HCl$ crystallises in slender, sparingly soluble prisms; the platinochloride was prepared; potassium permanganate oxidises thioammeline at the ordinary temperature, ammeline being formed.

Ammelide (Liebig's melanuric acid) acts either as a base or an acid; it may be prepared by boiling melam with concentrated potash or by heating it at 150° with concentrated sulphuric acid, or by heating ammeline at 160° with concentrated sulphuric acid, or by gently heating the ethyl salts of amidocyanuric or amidodithiocyanuric acids, or finally by the oxidation of thioammelide with potassium permanganate.

Ethyl amidothiocyanurate may be prepared by heating ethyl thiocyanurate with alcoholic ammonia at 180°, and extracting with ether, the diamido salt which is formed at the same time remaining undissolved. It is readily soluble in most of the usual solvents, although very sparingly in alcoholic ammonia, it melts at 112°, has basic properties, and crystallises in the form of a right rhombic prism terminated by a macrodome; $a : b : c = 0{\cdot}6692 : 1 : 0{\cdot}3912$.

Ethyl diamidothiocyanurate, obtained with the above compound, crystallises in prisms or needles, melts at 165°, and is insoluble in ether, but dissolves in alcohol, it has basic properties, but is readily converted into ammeline and ethyl hydrogen sulphide by the action of acids.

Amyl amidothiocyanurate, melting at 82°, and *amyl diamidothiocyanurate*, melting at 178°, were prepared from amyl thiocyanurate in a manner precisely similar to that employed in obtaining the ethyl salts. A. P.

Melam Compounds. By P. Klason (*J. pr. Chem.* [2], **33**, 285—289).—The crude melam obtained by Liebig consists of a mixture of melamine thiocarbamate, ammeline, ammelide, melam, and melem. Melamine is not formed from melam by the action of alkalis, but exists ready formed in the crude melam as melamine thiocyanate, and further Liebig's so-called pure melam consists of a mixture of melam and melem, $C_6H_7N_{10}$, with a varying proportion of mellone. The melam and melem may be best separated by boiling the mixture with a considerable quantity of very dilute hydrochloric acid, and adding excess of potash to the filtrate; the precipitate formed is nearly pure melam. As thus obtained, it forms a colourless powder, moderately soluble in acids, and insoluble in water, it is a feeble base, and occurs in crude melam as melam thiocyanate; by the action of alkalis or acids, it is converted entirely into ammeline and ammonia; it has the constitution $(NH_2)_2C_3N_3{\cdot}NH{\cdot}C_3N_3(NH_2)_2$.

Melem, which has been obtained by heating trithiocyanic acid to 360° (this vol., p. 324), appears to have the constitution

$$NH_2{\cdot}C_3N_3(NH)_2C_3N_3{\cdot}NH_2;$$

it may be obtained from Liebig's so-called pure melam by heating it with 4 parts of potassium hydroxide and 80 parts of water at 100° for 24 hours; by this means, the melam is converted into ammeline, whilst the melem is but little affected; melem is very similar in appearance to melam, and, like it, is a feeble base; by the action of concentrated acids or alkalis, it is entirely converted into ammelide and ammonia; this reaction may be best conducted by boiling melem with either concentrated potash or concentrated sulphuric acid until a small portion of the solution dissolves in water without the formation of any precipitate.

Mellone is converted by the action of alkalis first into cyameluric acid and ammonia; it probably has the constitution $(CN)_6(NH)_3$.

As cyameluric acid is formed from mellone and may be decomposed into cyanuric acid and ammonia, it appears to have the constitution $(HO)_2(CN)_3NH(CN)_3(OH)_2$. The author proposes to give the name of cyamellone to Liebig's mellone hydride, as it probably contains more cyanogen than mellone; it probably has the constitution $(C_3N_3)_3(NH)_3N$. A. P.

Combination of Methyl Alcohol with Cupric Sulphate. By de Forcrand (*Compt. rend.*, **102**, 551—553).—If finely powdered anhydrous cupric sulphate is agitated with pure, dry methyl alcohol,

the powder is converted into minute crystals having a bluish-green tinge, and the liquid acquires a bluish-green colour. The crystals have the composition $CuSO_4,2MeOH$, and are analogous to the compounds formed by methyl and ethyl alcohols with various metallic chlorides. If the blue solution is evaporated, it deposits similar crystals.

Heat of solution of the crystals (223·4 grams) at 8—10° = + 10·68 cal., and from this value and the known heats of solution of cupric sulphate and methyl alcohol it follows that $CuSO_4$ solid + $2CH_4O$ liquid = $CuSO_4,2CH_4O$ solid, develops + 9·76 cal. There is no appreciable thermal disturbance when a solution of cupric sulphate is mixed with a solution of methyl alcohol. No similar compounds are obtained with ethyl alcohol and the higher homologues.

It is evident that anhydrous cupric sulphate cannot be used as a test for the presence of water in methyl alcohol. C. H. B.

Formation of Closed Chains: Compounds of Diethylene Disulphide. By W. Mansfeld (*Ber.*, **19**, 696—702).—Husemann has shown that by the action of ethylene bromide on sodium sulphide an intermediate product is first formed, which is converted by heating into diethylene disulphide; this product he regarded as having the formula C_2H_4S (*Annalen*, **126**, 280). The author has reinvestigated this compound, which is a white, amorphous substance melting at 140°, not volatile, and insoluble in the ordinary solvents, and points out that its properties are incompatible with the assumption that it has a simpler formula than diethylene disulphide; he suggests that it probably has the formula $S<^{C_2H_4\cdot S}_{C_2H_4\cdot S}>C_2H_4$, analogous to that established by Hofmann for methylene sulphide ($C_3H_6S_3$).

By the action of trimethylene bromide on sodium sulphide a substance is obtained resembling that described above, except that it is not resolved into a simpler sulphide when heated; it is therefore most probably the triple compound $(C_3H_6)_3S_3$.

Diethylene disulphide is readily obtained by boiling the amorphous modification with phenol for several hours. The following additive products were prepared:—$C_4H_8S_2,EtI$, forming compact crystals. $C_4H_8S_2,MeI$, crystallising in rhombic prisms, $a : b = 0·898 : 1$; $C_4H_8S_2,2MeI$, crystallising in needles. A. J. G.

Products of the Oxidation of Mannitol with Potassium Permanganate. By F. Iwig and O. Hecht (*Ber.*, **19**, 468—473).—In a previous communication, the authors showed that in this reaction (in alkaline solution) formic, oxalic, and tartaric acids, and a substance which reduces Fehling's solution were formed (Abstr., 1882, 157); further investigation has shown that erythritic acid is also formed. The authors consider that mannitol is first oxidised to oxalic and erythritic acids, the last-named substance being then further oxidised to carbonic anhydride and formic, oxalic, and tartaric acids. If the oxidation is effected in acid solution, carbonic anhydride, formic acid, and erythritic acid are obtained.

The normal barium and calcium salts, $(C_4H_7O_5),Ba + 2H_2O$, and

$(C_4H_7O_5)_2Ca + 2H_2O$, and the basic barium salt of erythritic acid are described. It seems very probable, although not yet quite certain, that erythritic acid should be represented by the formula $C_4H_6O_5$, and not by the formula $C_4H_8O_5$, assigned to it by Lampartier and Sell.

A. J. G.

Anilides of Glucoses. By B. Sorokin (*Ber.*, **19**, 513).—Schiff described an anilide, $C_6H_7(OH)_5NPh$, obtained by heating dextrose with aniline; it formed a dark yellow, vitreous mass, decomposed by treatment with water or alcohol (*Annalen*, **154**, 30). Working under other conditions and at lower temperature, the author has obtained anilides of dextrose, levulose, and galactose, which are crystalline and dissolve in hot alcohol without decomposition. A. J. G.

Action of Hydrocyanic Acid on Dextrose. By H. Kiliani (*Ber.*, **19**, 767—772).—The constitutional formula ascribed to dextrose by Baeyer and by Fittig, namely, $CH_2(OH)\cdot[CH(OH)]_4\cdot CHO$, accounts best for the formation of gluconic and saccharic acids from dextrose by oxidation. On the other hand V. Meyer has shown (*Ber.*, **13**, 2343) that dextrose does not give the characteristic aldehyde reaction with magenta decolorised by sulphurous acid, and concludes that it is a ketonic alcohol. The formulæ proposed by Tollens (*Ber.*, **16**, 923), namely,

$$<^{CH(OH)\cdot CH(OH)\text{———}CH_2}_{CH(OH)\cdot CH(OH)\cdot CH(OH)}>O, \text{ or}$$

$$CH_2(OH)\cdot CH(OH)\cdot CH<^{O\text{———}CH(OH)}_{CH(OH)\cdot CH(OH)}>,$$

account for the formation of the above-mentioned oxidation products as well as the negative result obtained with magenta. The following experiments were made to determine whether dextrose is a ketonic alcohol or an anhydride:—When treated with hydrocyanic acid, the former should yield a compound containing an abnormal, the latter a compound containing a normal carbon-chain. 100 grams of anhydrous dextrose were heated in a closed vessel with 30 grams of water at 100° until a homogeneous syrup was obtained. When cold, the equivalent amount of a 60 per cent. solution of hydrocyanic acid was added, and the whole kept at the ordinary temperature. In about eight days the mixture became yellow; a considerable rise of temperature then took place and the colour changed to an intense red. It was then digested for 24 hours at 35°, by which time the odour of hydrocyanic acid had quite gone, and the product had a distinct odour of ammonia. It was now diluted with water treated with baryta, and evaporated to drive off all the ammonia. By precipitating the barium salt with sulphuric acid and evaporating the solution, a *lactone*, $C_7H_{12}O_7$, was obtained. This forms rhombic crystals, $a : b : c = 0{\cdot}3797 : 1 : 0{\cdot}8847$, readily soluble in water, insoluble in ether. The substance is lævorotatory. $[\alpha]_D = -55{\cdot}3°$. The *calcium salt*, $(C_7H_{13}O_8)_2Ca$, forms a gum. When boiled with concentrated hydriodic acid, the lactone is readily converted into a heptolactone; this, when further heated with hydriodic acid, yields only a trace of a heptylic

acid together with much hydrocarbon. The author intends synthesising normal heptolactone in order to identify the heptolactone prepared from dextrose. N. H. M.

Melitose from Eucalyptus Manna. By B. Tollens (*Annalen*, **232**, 201—204).—Eucalyptus melitose is optically inactive. It is completely decomposed by fermentation, and does not leave a residue of nonfermentable glucose, "eucalyn," as stated by Berthelot. Melitose is identical with the raffinose obtained from molasses and from cotton-seed meal. W. C. W.

Varieties of Starch. By F. W. Dafert (*Bied. Centr.*, 1886, 133—134).—In *Oryza glutinosa*, Kreusler and Dafert found a starch which behaves with iodine differently from rice-starch (this vol., p. 390). In the grains of *Panicum miliaceum glutinosum*, a Chinese plant, the starch is merely coloured yellow to red-brown by iodine, and never goes black with excess of iodine, but rather brown. Heat causes the colour to disappear, but the colour returns on cooling. Aqueous extracts do not contain dextrin. Bretschneider informs the author that there are two varieties of this plant in China, both botanically the same; but from the one, "Tsi," when mixed with water and baked a brittle mass may be made; whilst from the meal of the other, "Ihu," ordinary bread is formed. E. W. P.

Trimethylenediamine and Ethylenediamine Derivatives. By E. Fischer and H. Koch (*Annalen*, **232**, 222—228).—The method originally described by the authors (Abstr., 1884, 1289) for the preparation of trimethylenediamine yields better results than the modification proposed by Lellmann and Würthner (Abstr., 1885, 977). The aqueous solution of the base precipitates ferric hydroxide from a solution of ferric chloride. Mercuric chloride and Nessler's reagent give white precipitates. Cobalt, silver, and copper salts, form precipitates soluble in excess of the amine. Potassium bismuth iodide produces a red precipitate.

Trimethylenecarbamide, $C_3H_6<\overset{NH}{NH}>CO$, prepared by heating equivalent quantities of trimethylenediamine and ethyl carbonate in sealed tubes at 180° for six hours, crystallises in colourless needles or prisms. It melts at 260°, and dissolves in water. It is reprecipitated from the aqueous solution by the addition of concentrated alkalis. On oxidation with chromic acid mixture, a crystalline compound is formed which melts at 275°, and appears to have the composition $C_4H_4N_2O_2$.

Trimethylenediurethane, $C_3H_6(NH\cdot COOEt)_2$, is formed by the action of ethyl chlorocarbonate on trimethylenediamine in alcoholic ethereal solution. Trimethylenediamine hydrochloride is deposited, and the urethane is obtained on evaporating the filtrate. It is soluble in ether, alcohol, chloroform, and in dilute acids. From the acid solutions, it is reprecipitated by alkalis. The urethane melts at 42°, and distils at 210° under 30 mm. pressure. It is decomposed by distil-

lation under the ordinary atmospheric pressure, the chief products being trimethylenecarbamide and ethyl carbonate.

Trimethylenedicarbamide, $C_3H_6(NH{\cdot}CONH_2)_2$, is best prepared by the action of trimethylenediamine hydrochloride on freshly precipitated silver cyanate. The compound is freely soluble in water, sparingly soluble in cold alcohol. It crystallises in needles, and melts at 182°.

Ethylenecarbamide, $C_2H_4 : N_2H_2 : CO$, melts at 131°. It crystallises in needles, and dissolves freely in water and in hot alcohol. Ethylenedicarbamide, $C_2H_4(NH{\cdot}CONH_2)_2$, has been described by Volhard under the name of ethylenecarbamide.

Ethylenediurethane, $C_2H_4(NH{\cdot}COOEt)_2$, melts at 112°, and dissolves freely in alcohol and ether. It is deposited from a hot aqueous solution in colourless needles. W. C. W.

Penta- and Tetra-methylenediamine. By A. Ladenburg (*Ber.*, **19**, 780—783; compare this vol., p. 139).—Pentamethylenediamine boils at 178—179°, and solidifies when cooled by a freezing mixture. The *aurochloride* crystallises in prisms, readily soluble in water. The *picrate* and the *mercuriochloride* are readily soluble; the periodide forms almost black crystals.

Tetramethylenediamine, $C_4H_8N_2H_4$, is prepared by reducing ethylene cyanide with sodium and alcohol; the yield is not so good as in the case of pentamethylenediamine. The free base is obtained from the hydrochloride by distilling the latter with powdered sodium hydroxide and some concentrated caustic potash. It is a colourless liquid, boiling at 158—160°; when cooled, it readily solidifies and melts then at 23—24°. It has a strong odour of piperidine. When exposed to the air, it fumes; it absorbs carbonic anhydride quickly. The *hydrochloride*, $C_4H_8N_2H_4,2HCl$, forms soft, tabular crystals, generally somewhat reddish. The *aurochloride* forms yellow prisms, and is sparingly soluble; the *picrate* separates from its solution in chloroform in thin, matted yellow needles, with a silky lustre. The *sulphate* and *platinochloride* are also described.

The crude tetramethylenediamine hydrochloride was found to contain pyrrolidine (Ciamician and Magnaghi, Abstr., 1885, 1243). Benzyl cyanide is readily converted by the action of sodium and alcohol into phenylethylamine; this boils at 194·5—195° (not 193°, as usually given). Propylamine may be obtained from ethyl cyanide in a similar manner. N. H. M.

Diacetonamine. By H. Weil (*Annalen*, **232**, 206—214).—Heintz has shown (this Journal, 1877, ii, 878) that diacetonamine unites with hydrocyanic acid to form a nitrile, which, on hydrolysis with hydrochloric acid, yields a neutral substance, $C_7H_{13}O_2N$, the anhydride of amidotrimethylbutyllactic acid, or *dioxytrimethylpyrroline*. The nitrile is best prepared by adding double the theoretical amount of hydrocyanic acid to a concentrated solution of diacetonamine hydrochloride. After some hours, ammonia is added to the mixture. Dihydroxytrimethylpyrroline is obtained by boiling the liquid with an equal volume of strong hydrochloric acid for six hours in a

flask with a reflux condenser, and then evaporating in a vacuum. The product is treated with boiling alcohol to remove ammonium chloride. On evaporating the alcoholic solution, a crystalline mass is obtained, which consists chiefly of dihydroxytrimethylpyrroline. It also contains a small quantity of *amidotrimethylbutyllactic acid*, which is insoluble in alcohol and ether. This acid is deposited from its aqueous solution in colourless prisms. It melts at 210°, and splits up at a higher temperature into water and dihydroxytrimethylpyrroline; this substance melts at 202°. It is soluble in hot alcohol and in water, but is precipitated unaltered from its aqueous solution by concentrated alkalis. Phosphoric chloride attacks it energetically. If the product of the reaction is poured into water, a crystalline compound, $C_7H_{12}ONCl$ (melting at 155°), is obtained.

Dihydroxytrimethylpyrroline is converted into the anhydro-compound, $C_7H_{11}NO$, by the action of strong sulphuric acid at 100°. The anhydro-compound crystallises in needles; it melts at 141·5° and boils about 240°. It is freely soluble in water, alcohol, and ether. It is not attacked by methyl iodide, nor does it yield a nitrosamine. By the action of metallic sodium on the alcoholic solution, it is converted into *hydroxytrimethylpyrroline*, $C_7H_{13}ON$; this melts at 79·5° and boils at 220°, but sublimes at a low temperature. It dissolves freely in water, ether, alcohol, benzene, and light petroleum. The *nitroso*-compound, $C_7H_{12}N_2O_2$, melts at 98°.

On distillation with zinc-dust, hydroxytrimethylpyrroline yields an oily liquid, probably trimethylpyrrolidine, $C_7H_{15}N$. The oil is sparingly soluble in water, but dissolves readily in alcohol and ether. The aqueous solution turns red on exposure to the air. With mercuric chloride, it yields a white precipitate. W. C. W.

Hydroxyphosphinic Acids. By W. Fossek (*Monatsh. Chem.*, **7**, 20—39; compare Abstr., 1885, 504). — Hydroxyisoamylphosphinic acid, when treated with phosphorus pentachloride, yields a trichloride, $C_4H_9{\cdot}CHCl{\cdot}POCl_2$. This is an oil, boiling between 106° and 109°, under a pressure of 12 mm. When dissolved in absolute alcohol, and the solution evaporated in a vacuum, *ethylic amylchlorophosphinate*, $C_4H_9{\cdot}CHCl{\cdot}PO(OC_2H_5)_2$, is formed. When treated with water, it loses two atoms of chlorine only, forming *amylchlorophosphinic acid*, $C_4H_9{\cdot}CHCl{\cdot}PO(OH)_2$, a yellow, crystalline, hygroscopic mass. This acid forms a normal calcium salt, $C_4H_9{\cdot}CHCl{\cdot}PO_3Ca$, which is equally soluble in cold and hot water. *Isoamylphosphinic acid*, $C_4H_9{\cdot}CH_2{\cdot}PO(OH)_2$, prepared by reducing hydroxyisoamylphosphinic acid with hydriodic acid in sealed tubes, forms brilliant white plates, melting at 160—162°; the *silver* salt, $C_4H_9{\cdot}CH_2{\cdot}POAg_2$, is precipitated on adding silver nitrate to a neutral solution of the acid. Hydroxyisobutylphosphinic acid gives the corresponding acid when reduced with hydriodic acid.

Hydroxyheptylphosphinic acid, $C_6H_{13}{\cdot}CH(OH){\cdot}PO(OH)_2$, prepared in the same way as the acids previously described, forms large, monoclinic crystals, $a:b:c = 1{\cdot}8442:1:1{\cdot}9574$. It begins to soften at 165°, and melts to a dark brown liquid at 185°. The *calcium* salt, $C_7H_{15}PO_4Ca$, is obtained as a white precipitate. When reduced with

hydriodic acid, it yields the corresponding *heptylphosphinic acid*. This melts at 106°, and is soluble in ether, alcohol, and light petroleum.

Hydroxypropylphosphinic acid, $CHEt(OH)\cdot PO)OH)_2$, forms brilliant, monosymmetric plates, $a : b : c = 0{\cdot}876 : 1 : ?$; it melts at 162°, and is easily soluble in water, alcohol, and ether, insoluble in benzene. The calcium and barium salts are described.

Hydroxyethylphosphinic acid, $CHMe(OH)\cdot PO(OH)_2$, forms a white, crystalline mass; it melts at 74—78°, and begins to decompose at 100°.

Hydroxybenzylphosphinic acid, $CHPh(OH)\cdot PO(OH)_2$, is obtained as a crystalline crust. It is soluble in water, ether, alcohol, insoluble in benzene. It melts at 173°. The acid and normal barium salts are described.

Hydroxyphenanthraquinonephosphinic acid,

$$C_6H_4<\begin{matrix}C_6H_4\\-CO-\end{matrix}>C(OH)\cdot PO(OH),$$

is prepared by digesting phenanthraquinone with excess of phosphorus trichloride. It forms flesh-coloured flakes, which are crystalline under the microscope; it melts at 125—128°. It is easily soluble in water, alcohol, ether, and glacial acetic acid to red liquids. The *calcium* salt, $C_{14}H_9PO_5Ca$, separates out in deep-green flocks on addition of calcium chloride to a solution of the acid. When oxidised with potassium permanganate in a slightly acid solution, this acid splits up into phenanthraquinone and phosphoric acid.

G. H. M.

Magnesium Acetate. By Kubel (*Arch. Pharm.* [3], **24**, 158—161).—The salt was prepared by adding a slight excess of magnesium carbonate to aqueous acetic acid (15 per cent.), boiling some time, filtering and concentrating until a gum-like skin forms on the surface. From the syrupy mass thus produced, crystals can be readily obtained by adding a few crystals of the salt. Crystals, several centimetres long, are frequently obtained, of a columnar shape, with truncated ends, belonging to the monoclinic system. The salt has the composition $Mg(C_2H_3O_2)_2 + 4H_2O$; it melts about 80°; at a higher temperature water and acetic acid and finally acetone are driven off, and a greyish mass of magnesia is left. It is very soluble in water and alcohol. A table of specific gravities of the aqueous solution is given.

J. T.

Iodopropargylic Acid. By F. Stolz (*Ber.*, **19**, 536—545; compare Abstr., 1885, 1198).—*Bromiodacrylic acid*, $CHBr : CI\cdot COOH$, is prepared by boiling propargylic acid with a slight excess of iodine bromide in ethereal solution for about an hour. The residue obtained on evaporating the ether, is decolorised with sulphurous acid and crystallised from ether; it is then pressed between filter-paper, dissolved in hot water in presence of animal charcoal, and the solution evaporated in a vacuum over sulphuric acid. It is readily soluble in alcohol, ether, and chloroform, &c., and melts at 71°. When boiled

with silver bromide in alcoholic solution, it is converted into α-β-dibromacrylic acid.

The bromiodoacrylic acid previously described (*loc. cit.*), and that prepared by Hill (Abstr., 1879, 616), have respectively the following constitutional formulæ ascribed to them: CHI : CBr·COOH and ClBr : CH·COOH.

Chloriodacrylic acid, $C_2HClI\cdot COOH$, is obtained by boiling an ethereal solution of propargylic acid with a slight excess of iodine chloride for some hours. The product is treated with sulphurous acid, pressed between filter-paper, and crystallised from water. It forms groups of lustrous needles melting at 72°; it is readily soluble.

Di-iodochloracrylic acid, $C_2I_2Cl\cdot COOH$, is obtained by the action of iodine chloride on iodopropargylic acid. It crystallises from water in lustrous plates, which become rose-coloured when exposed to light. It melts at 143°. The constitution of the compound is probably CI_2 : CCl·COOH.

Chlorobromiodoacrylic acid, $C_2ClBrI\cdot COOH$, is formed when a solution of iodopropargylic acid in chloroform is gradually added to a cooled solution of bromine chloride in chloroform. It crystallises from water in lustrous plates resembling potassium chlorate, melts at 128—129°, and dissolves readily in water. alcohol, and ether. It is not identical with the acid obtained by Mabery and Lloyd (Abstr., 1882, 1049), by the action of iodine chloride on bromopropargylic acid.

Iodopropargylic acid is not changed by boiling with silver bromide, or by prolonged contact with strong sulphuric acid. Alcohol saturated with hydrogen chloride has no action on the ethyl salt.

β-Bromacrylic acid, CHBr : CH·COOH, is prepared by dissolving propargylic acid in slightly fuming hydrobromic acid. It melts at 115°, and is identical with the acid obtained by Wallach (Abstr., 1878, 404), by the reduction of trichlorethylidene tribromolactate. The mother-liquor, obtained in preparing this substance, yielded a mixture of acids (probably containing dibromopropionic acid), melting at 53—70°. This would account for the melting point (53°) ascribed to β-bromacrylic acid by Baudrowsky (*Ber.*, **15**, 2702), who prepared it in the manner described above.

When propargylic acid is treated with concentrated hydriodic acid, an iodacrylic acid, $C_3H_3IO_2$, is obtained, which crystallises in large colourless quadrangular prisms, melting at 65°; it is apparently a physical isomeride of Baudrowsky's iodacrylic acid (m. p. 140°; *loc. cit.*), which is formed when dilute hydriodic acid is employed.

N. H. M.

Breaking up of the Lactone-ring by the Action of Alcohol and Halogen Hydro-acids. By J. Bredt (*Ber.*, **19**, 513—516).—The halogen hydro-acids readily react with some lactones, forming the corresponding halogen substituted acids; other lactones, however, are not decomposed by treatment either with the aqueous or gaseous hydro-acids; in some cases, however, if alcohol is added, the lactone is decomposed. Isocaprolactone, for example, if dissolved in absolute alcohol and saturated with hydrogen chloride or bromide, is converted into *ethyl γ-chlor-* or *γ-bromisocaproate*. The chloro-compound boils

without decomposition at 88° under 12 mm. pressure; heated at higher pressures it is resolved into hydrogen chloride and ethyl pyroterebate. The bromo-compound when heated is decomposed into ethyl bromide and the original lactone. The results of other observers have, however, shown that this reaction is by no means general for the lactones. A. J. G.

Formation of Levulinic Acid from Various Substances in Reference to the Detection of Carbohydrates. By C. Wehmer and B. Tollens (*Ber.* **19**, 707—708).—In confirmation of the suggestion of Kent and Tollens (Abstr., 1885, 647) that all true carbohydrates yield levulinic acid when heated with mineral acids, the authors have investigated the products formed by boiling various substances with hydrochloric acid with the following results:—Levulinic acid is obtained from starch, dextrose, sorbin, salicin, and amygdalin, and also in distinct quantity from chondrin; it is not obtained from inosite, isosaccharin, phloroglucinol, santonin, carmin, tannic acid, piperic acid, caseïn, fibrin, and the *ligamentum nuchæ*.

A. J. G.

Platoso-oxalic Acid. By H. G. Söderbaum (*Bull. Soc. Chim.*, **45**, 188—193).—Sodium platoso-oxalate, $Pt(OCO{\cdot}COONa)_2$, may be prepared by heating sodium platinochloride with an equal weight of soda and extracting the residue with water, when a yellow powder, $Na_2O,3PtO_2,6H_2O$, remains; this when washed with water and heated with $1\frac{1}{2}$ parts of crystallised oxalic acid, gives off carbonic acid and forms an intensely blue-coloured solution, from which, on cooling, slender, brown crystals having a metallic lustre are deposited. On washing these on a filter with boiling water, the first liquid passing through is yellow, the latter part of the washings are greenish or blue, and the last portions of a reddish-brown colour; the latter on cooling deposit hair-like, copper-coloured crystals of sodium platoso-oxalate, whilst the first part of the washings deposits citron-yellow prisms of an isomeric salt; the intermediate portions depositing mixtures of these two isomerides. By treating either of these salts with silver nitrate, a yellowish-white precipitate of microscopic crystals of the silver platoso-oxalate is formed.

The free acid obtained by decomposing the silver salt with hydrochloric acid forms a red crystalline mass having a metallic lustre; after drying at 100°, it has the composition $PtC_4O_8H_2 + 2H_2O$; it dissolves in water with an indigo-blue colour which turns into yellow on heating or dilution with water, the blue colour being, however, restored by cooling or concentration. Salts of other metals prepared from the brown sodium salt are of a brown, greenish, or blue colour, whilst the isomeric salts prepared from the yellow sodium salt are yellow or orange; the free acid generally forms the darker coloured salts, but by repeated recrystallisation the yellow salts may be obtained. Many metals belonging to the zinc-group form dark coloured salts most readily, whilst others, such as silver, form the yellow salts in preference, and a third class form either isomeric variety with equal facility. The dark salts are usually less soluble than the yellow, their sp. gr. is also lower, and they frequently contain

a smaller amount of water of crystallisation. The salts of platoso-oxalic acid are in general but sparingly soluble in cold water and dilute acids; they are insoluble in alcohol, but dissolve readily in hot water. They mostly contain water of crystallisation which they lose at 100°. They are generally decomposed when heated to about 110—115°. The dark and yellow coloured salts of the alkalis, the alkaline earths, many of the rare metals, and nickel, lead, iron, manganese, cadmium, copper and mercury, are described in detail. A. P.

Action of Nitric Acid on Substituted Malonic Acids. By A. P. N. Franchimont (*Rec. Trav. Chim.*, **4**, 393—401).—The author, in continuation of his experiments on the action of nitric acid on acids of the oxalic series, describes experiments to show that only mono-substituted derivatives of malonic acid are decomposed by nitric acid, whilst di-substituted derivatives, as also trimethylene- and tetramethylene-dicarboxylic acids are unaltered. Thus isosuccinic, ethyl-α- and β-propyl, and amyl-malonic acid yield a quantity of carbonic anhydride corresponding with the destruction of both the carboxyl-groups, whilst allylmalonic acid yields at first a considerable quantity of oxides of nitrogen, and subsequently the same relative quantity of carbonic anhydride. Dimethyl-, diethyl-, and diallyl-malonic acids yield no carbonic anhydride. The stability of trimethylene- and tetramethylene-dicarboxylic acids in presence of nitric acid offers a further confirmation of Perkin's view regarding their constitution (Trans., 1885, 801—855). V. H. V.

Methylhydroxyglutaric Acid and the corresponding Lactonic Acid. By J. Block and B. Tollens (*Ber.*, **19**, 706—707).—The lactonic acid, $C_6H_8O_4$, obtained from levulinic acid as previously described (Abstr., 1885, 1202), distils in a vacuum at 200° as a thick oil which soon becomes crystalline; when heated with concentrated sulphuric acid, it is reconverted into levulinic acid.

Cyanovalerolactone, $C_6H_7NO_2$, is obtained by the action of hydrogen cyanide on levulinic acid; it is crystalline, and melts at 32°. A nitrogenous compound melting at 132° is formed at the same time.

A. J. G.

Sodium Ammonium and Sodium Potassium Racemates. By G. Wyrouboff (*Compt. rend.*, **102**, 627—629).—A criticism of Bichat's paper (this vol., p. 446). The author calls attention to his own paper on the same subject (this vol., p. 445). The inorganic particles to which Bichat refers, simply serve to produce crystallisation in solutions which have become supersaturated. The splitting up of the sodium ammonium and sodium potassium racemates is a question of solubility, which is a function of the temperature (*loc. cit.*).

C. H. B.

Crystallisation of Sodium Ammonium Paratartrate. By J. Joubert (*Compt. rend.*, **102**, 507—508).—If a solution of sodium ammonium paratartrate is allowed to evaporate spontaneously in a current of carefully filtered and dry air, it deposits large, regular crystals of the paratartrate which show no hemihedral faces, and are sometimes several centimetres long. C. H. B.

The Thiophen-group. By V. Meyer (*Ber.*, **19**, 628—632).—α- and β-Thiophenic acids both seem to have the same constitution, [COOH = 2], but certain of their properties are quite different. The derivatives of both acids show complete identity in crystalline form, solubility, melting point, &c. (Bonz, Abstr., 1885, 1206; Meyer, *ibid.*, 1207), but on reconversion into the acids, those derivatives prepared from the α-acid yield the α-acid exclusively; those from the β-acid, again yield β-thiophenic acid. The seeming identity of the derivatives has been found to hold good for the amides, carbamide-derivatives, nitriles, and hydroxylamine compounds, as well as those previously described (*loc. cit.*).

The greater part of the paper is occupied by a summary of the results of investigations on the thiophen-group recently made by the author's scholars (see following Abstracts).

The author and A. Kaiser have endeavoured to synthesise a closed-chain compound containing 1 sulphur and 5 carbon atoms, by treating with phosphorus trichloride the compound $S(CH_2{\cdot}CH_2{\cdot}OH)_2$ obtained from ethylene chlorhydrin, when it yields a crystalline substance of the formula $S(CH_2{\cdot}CH_3Cl)_2$; it was thought that by treating this with ethyl sodomalonate, a compound, $S<^{CH_2{\cdot}CH_2}_{CH_2{\cdot}CH_2}>C(COOEt)_2$, would be obtained, but the product of the reaction has not yet been obtained in a state fit for examination. A. J. G.

Trichlorothiophen and its Derivatives. By J. Rosenberg (*Ber.*, **19**, 650—652).—*Trichlorothiophen*, C_4SHCl_3 [? 2 : 3 : 4], is obtained by the action of chlorine on the bye-products of the preparation of dibromothiophen; the product is treated with alcoholic potash and finally submitted to repeated fractional distillation to separate it from the far larger quantity of tetrachlorothiophen formed simultaneously. It is a heavy oil, of odour similar to that of chlorobenzene, boils at 206—207° (uncorr.), and gives the indophenine reaction.

Trichlorothiophensulphonic anhydride, $(C_4SCl_3{\cdot}SO_2)_2O$, is obtained by the action of pyrosulphuric acid on trichlorothiophen; it crystallises in white, lustrous needles, and is nearly insoluble in water, alcohol and ether, more soluble in benzene; long-continued boiling with water or alkalis converts it into the corresponding sulphonic acid or its salts.

Nitrotrichlorothiophen, $C_4SCl_3{\cdot}NO_2$, crystallises in reddish-yellow, interlaced needles, melts at 86°, and is readily soluble in ether and benzene, sparingly in alcohol. A. J. G.

Limited Oxidation of Ethylthiophen. By E. Schleicher (*Ber.*, **19**, 671—672).—Ethylthiophen when treated in alkaline solution with a small quantity of dilute permanganate, yields β-thiophenic acid and a little acetothiënone. This corresponds with the incomplete oxidation of ethylbenzene, which has been shown to yield much benzoic acid with a small quantity of acetophenone (Friedel and Balsohn, Abstr., 1880, 469). A. J. G.

Isopropylthiophen. By E. Schleicher (*Ber.*, **19**, 672—674).—*Isopropylthiophen*, $C_4SH_3Pr^{\beta}$, is obtained by adding aluminium chlo-

ride in small portions to a mixture of thiophen and isopropyl bromide dissolved in light petroleum. It is an oil of intense odour, boils at 153—154° (corr.), and has a sp. gr. of 0·9695 at 16°. A trace of the oil when mixed with phenanthraquinone in glacial acetic acid solution and treated with sulphuric acid, gives an intense violet-red coloration, but this becomes discoloured on mixing it with water, and ether does not extract a violet colouring matter from the aqueous solution; this reaction distinguishes it from all the homologues of thiophen hitherto described. A. J. G.

Diethylthiophen. By F. Muhlert (*Ber.*, **19**, 633—636).—*Diethylthiophen*, $C_4SH_2Et_2$, is prepared by adding 20 grams of iodoethylthiophen and 20 grams of ethyl iodide to 6 grams of finely divided sodium placed under ether in a vessel surrounded by a freezing mixture. It boils at 181° (corr.), and has a sp. gr. = 0·962 at 14° (water at 14° = 1). Bromo- and nitro-derivatives were prepared, but in quantity too small for purification.

Acetodiethylthiënone, $C_4SHEt_2{\cdot}COMe$, is prepared by adding a mixture of acetic chloride, diethylthiophen, and light petroleum to aluminium chloride suspended in light petroleum, and decomposing the product with water. It is an oil boiling without decomposition at about 250°. When treated with hydroxylamine, it yields the *acetoxime* $C_4SHEt_2{\cdot}CMe : NOH$, as a yellow oil which can be distilled unchanged. A. J. G.

Octyl-derivatives of Thiophen. By E. A. v. Schweinitz (*Ber.*, **19**, 644—649).—*Octylthiophen*, $C_4SH_3{\cdot}C_8H_{17}$, is prepared by the action of sodium on a mixture of normal octyl bromide and iodothiophen in ethereal solution; it is an oil boiling at 257—259°, sp. gr. = 0·8118 compared with water at 20·5°, is readily soluble in ether, and resembles octylbenzene (this vol., p. 540) in taste and odour. *Bromoctylthiophen*, $C_4SH_2Br{\cdot}C_8H_{17}$, boils at 285—290°, and solidifies at 5°. *Iodoctylthiophen*, $C_4SH_2I{\cdot}C_8H_{17}$, prepared by the action of mercuric oxide and iodine on octylthiophen diluted with an equal volume of light petroleum, is a yellow oil solidifying at 0°, and has sp. gr. 1·2614 compared with water at 20°. A few yellow crystals, probably of the diiodo-compound, are obtained at the same time. Attempts to prepare an octylthiophensulphonic acid were unsuccessful, β-thiophendisulphonic acid being formed.

Octylacetothiënone, $C_8H_{17}{\cdot}C_4SH_2{\cdot}COMe$, is obtained by the action of acetic chloride and aluminium chloride on octylthiophen diluted with light petroleum. It is an oil of garlic-like odour, boils at 350—355°, and gives a white, crystalline derivative with hydroxylamine.

Octyldiacetothiënone, $C_8H_{17}{\cdot}C_4SH(COMe)_2$, is obtained at the same time as the monaceto-compound, or is exclusively formed if excess of acetic chloride is employed; it forms a yellow, syrupy liquid which solidifies on strong cooling, is readily soluble in alcohol, insoluble in ether, and, with hydroxylamine, yields a compound crystallising in tufts of white needles, and melting at 58°.

Octylthiophendicarboxylic acid, $C_8H_{17}{\cdot}C_4SH(COOH)_2$, is prepared by oxidising the diaceto-compound with an alkaline solution of potas-

sium permanganate. It is obtained on evaporation of its ethereal solution as an unctuous, yellowish-white mass composed of microscopic needles; it melts at 185°, and is nearly insoluble in cold water. The barium salt, $C_{14}H_{18}SO_4Ba + 1\frac{1}{2}H_2O$, the copper salt with $2\frac{1}{2}$ mol. H_2O, and the silver salt with 3 mol. H_2O are described.

Methyloctylthiophen, $C_8H_{17}\cdot C_4SH_2Me$ [C_8H_{17} : Me = 2 : 5], was obtained both by the action of sodium on a mixture of iodothiotolen and octyl bromide, and on a mixture of iodoctylthiophen and methyl iodide, the supposition that isomeric substances might be formed in the two reactions being negatived. It is a colourless oil, boiling at 270°, and solidifying when well cooled to a crystalline mass melting at 10°. The *monobromo*-derivative, $C_8H_{17}\cdot C_4SHMeBr$, melts at 20°.

A. J. G.

β-Thiophenaldehyde and β-Thiënyl Alcohol. By A. Biedermann (*Ber.*, **19**, 636—640).—Acetothiënone is best prepared by slowly adding 150 grams of aluminium chloride to a solution of 50 grams of thiophen and 55 grams of acetic chloride in 500 grams of light petroleum; after the reaction has ceased, the mixture is heated until hydrogen chloride is no longer evolved; the petroleum is poured off, the residue again treated with acetic chloride (5 grams) and aluminium chloride, and finally the solid product is decomposed with ice-cold water and distilled with steam. The yield is above 90 per cent. of the theoretical, whilst by the old method not more than 40 per cent. was obtained.

The preparation of β-thiophenaldehyde, by oxidising acetothiënone to thiënylglyoxylic acid and then heating this alone, has already been described by Peter (Abstr., 1885, 764). The pure aldehyde is a pale-yellow oil, boiling at 198° (corr.); it slowly oxidises to β-thiophenic acid when exposed to air. The phenylhydrazine compound,

$$C_4SH_3\cdot CH : N_2HPh,$$

crystallises in yellow needles and melts at 119° (uncorr.).

Thiënyl alcohol, $C_4SH_3\cdot CH_2\cdot OH$, is prepared by shaking β-thiophenaldehyde with concentrated aqueous potash, and after the lapse of 12 hours dissolving the solid product in water and extracting with ether, by which the alcohol is separated from the potassium thiophenate simultaneously formed. It is a colourless liquid, of odour resembling that of benzyl alcohol, and boils at 207° (corr.). When saturated with hydrogen chloride, it is slowly converted into *thiënyl chloride*, $C_4SH_3\cdot CH_2Cl$, a colourless liquid, boiling at 175°.

A. J. G.

Synthesis of Thiotenol (Hydroxythiotolen) and Thiotolen. By W. Kues and C. Paal (*Ber.*, **19**, 555—557).—*Thiotenol*,

$$C_4SH_2Me\cdot OH,$$

is prepared by heating an intimate mixture of levulinic acid (3 parts) and phosphorus pentasulphide (2 parts) in a retort at 130—140°. A yellow, oily distillate is obtained consisting chiefly of thiotenol; this is distilled with steam and the distillate further purified by distilling in a partial vacuum; or it is dissolved in soda, filtered, and the filtrate made acid and distilled with steam. The yield of pure substance is

about 30 per cent. of the theoretical. It is an almost colourless, mobile oil, having a peculiar, disagreeable odour, sparingly soluble in water, and miscible in all proportions with alcohol and ether; caustic alkalis dissolve it readily. It is rather unstable, and soon becomes brown when exposed to light and air. It boils without decomposition at 85° under 40 mm. pressure, and solidifies in a mixture of solid carbonic anhydride and ether. When treated with isatin and sulphuric acid, it gives a Bordeaux red coloration. The *acetyl-derivative*, $C_4SH_2Me{\cdot}OAc$, is a yellowish oil, boiling at 208—212°; it gives the same colour reaction with isatin and sulphuric acid as thiotenol does.

Thiotolen is obtained by heating 1 part of levulinic acid with $1\frac{1}{2}$ parts phosphorus trisulphide, as in the preparation of thiotenol. The distillate is treated with caustic soda, and the oil purified by distilling it over sodium. The yield of thiotolen is 15 per cent. of the theoretical amount. The alkaline solution is acidified and distilled with steam; the thiotenol thus obtained (amounting to 25—30 per cent. of the theoretical) can be readily converted into thiotolen by the action of phosphorus trisulphide. It is identical with Meyer and Kreis's methylthiophen (Abstr., 1884, 1131). N. H. M.

Action of Acetic Chloride on Halogen-derivatives of Thiophen. By L. Gattermann and M. Römer (*Ber.*, **19**, 688—695).—These experiments were commenced in the hope of obtaining a γ-thiophenic acid by acetylising β-β-dibromothiophen and so obtaining a dibromo-γ-acetothiënone, which on oxidation and debromination would yield the γ-acid. It was found, however, that the acetyl-group displaces one of the bromine-atoms, yielding the same compound as is obtained by acetylising the monobromo-derivative.

Bromacetothiënone, $C_4SH_2Br{\cdot}COMe$, is obtained by the action of acetic chloride, aluminium chloride, on either mono- or di-bromothiophen dissolved in light petroleum; it crystallises in compact, colourless needles, melts at 94°, distils readily with steam, and is moderately soluble in hot alcohol. The phenylhydrazine compound, $C_4SH_2Br{\cdot}CMe : N_2HPh$, crystallises in pale-yellow tables, melts at 122°, and is sparingly soluble in hot alcohol.

Bromothiophenic acid, $C_4SH_2Br{\cdot}COOH$, prepared by the oxidation of bromacetothiënone with an alkaline solution of potassium permanganate, crystallises in lustrous, colourless needles, melts at 139·5°, sublimes readily in colourless, nacreous needles, and is readily soluble in alcohol and ether, very sparingly in cold water. A flocculent intermediate oxidation product, probably bromothiënylglyoxylic acid, is also formed in small quantity.

Tribromothiophen is not acetylised when treated with acetic and aluminium chlorides; a small quantity is converted into tetrabromothiophen.

Iodacetothiënone, $C_4SH_2I{\cdot}COMe$, prepared by the action of acetic and aluminium chlorides on mono- or di-iodothiophen, crystallises in long, colourless needles, melts at 129°, and distils readily with steam. The phenylhydrazine compound crystallises in yellow tables and melts at 134° with decomposition. *Iodothiophenic acid*, $C_4SH_2I{\cdot}COOH$,

crystallises in colourless silky needles, melts at 131°, and sublimes readily in lustrous tables.

Chloracetothiënone, $C_4SH_2Cl{\cdot}COMe$, prepared from chlorothiophen, and seemingly also from dichlorothiophen, crystallises in large, colourless, rhombic tables, melts at 52°, and distils readily with steam. The phenylhydrazine compound crystallises in golden-yellow tables, and melts at 108° with decomposition. *Chlorothiophenic acid*, $C_4SH_2Cl{\cdot}COOH$, crystallises in colourless needles, melts at 140°, sublimes readily, and is sparingly soluble in hot water.

A. J. G.

Acetyl- and Carboxyl-derivatives of Thiophen. By R. Demuth (*Ber.*, **19**, 679—688).—γ-Methylacetothiënone (this vol., p. 288) was treated with potassium permanganate in quantity sufficient to convert it into a dicarboxylic acid, but it was found that it was only converted into a monocarboxylic acid. *γ-Thiotolenic acid*, $C_4SH_2Me{\cdot}COOH$, thus obtained, crystallises in very slender, interlaced needles, melts at 144—145°, sublimes in feathery needles, and is less soluble in water than the isomeric β-acid. The silver and calcium salts are described. When oxidised with excess of permanganate, a product was obtained consisting of much unaltered acid, resinous substances, and a compound crystallising in pale-yellow needles which sublime with decomposition at about 270°. It could not be ascertained whether this was the dicarboxylic acid sought for, as the amount obtained was too small for analysis.

When iodethylthiophen [2 : 5] dissolved in light petroleum is treated with acetic chloride and aluminium chloride, much iodine separates, and the product consists of a mixture of 2 : 5 ethylacetothiënone (5 mols.) and iodethyl-γ-acetothiënone (3 mols.), which could not be separated as it decomposes on distillation. A similar result was obtained on acetylising bromethylthiophen, although the proportion of bromethyl-γ-acetothiënone formed was much larger. These products were then submitted to oxidation (by which they are in great part destroyed), and the yellowish masses obtained reduced with sodium amalgam, when they yielded only the known 2 : 5 thiophendicarboxylic acid, and not as was hoped an isomeric β-γ-dicarboxylic acid.

Bromethylthiophen, C_4SH_2EtBr, is obtained by the action of bromine-water on ethylthiophen, care being taken that no rise of temperature occurs. It is a pale-yellow oil, boiling at 195° with some decomposition.

A. J. G.

Isobutyrothiënone and Propiothiënone. By K. Krekeler (*Ber.*, **19**, 674—679).—*Isobutyrothiënone*, $C_4SH_3{\cdot}COPr^{\beta}$, prepared by the action of isobutyric chloride on thiophen in presence of aluminium chloride, is a colourless, heavy oil, boiling at 232° (corr.). The corresponding *acetoxime* crystallises in white, nacreous plates, and melts at 107—108°. The phenylhydrazine compound is an oil showing no characteristic properties. The limited oxidation of the ketone yielded β-thiophenic acid. Isobutyrothiënone dissolves in concentrated sulphuric acid in the cold with violet coloration, and on dilution with water is precipitated unchanged, but on heating the solution, iso-

butyric and thiophensulphonic acids are formed, a part of the latter acid being further converted into the disulphonic acid. This peculiar reaction seems to be general for the ketones of the thiophen series.

Propiothiënone, $C_4SH_3{\cdot}COEt$, prepared in manner similar to the isobutyro-compound, is a colourless oil heavier than water, and boils at 228° (corr.). It yields β-thiophenic acid when oxidised, and is converted into propionic and thiophensulphonic acids when heated with sulphuric acid. The *acetoxime*, $C_4SH_3{\cdot}CEt : NOH$, crystallises in lustrous white plates, and melts at 55—56°.

When acetophenone is heated with sulphuric acid, benzoic and benzenesulphonic acids are formed; acetic acid could not be detected, the acetyl-group being, it would seem, completely oxidised.

A. J. G.

Ketones of the Thiophen-group. By E. Schleicher (*Ber.*, **19**, 660—670).—Acetoethylthiënone when perfectly pure is an oil of fruity odour, which boils at 248—250° (corr.), and has a sp. gr. = 1·0959 at 20° (water at 20° = 1). The phenylhydrazine compound, $C_4SH_2Et{\cdot}CMe : N_2HPh$, crystallises in tufts of pale-yellow needles, melts at 68°, and decomposes readily in presence of moisture. When gently heated with concentrated sulphuric acid, acetoethylthiënone is converted into acetic acid and ethylthiophen-sulphonic and -disulphonic acids (comp. Krekeler, preceding Abstract); by the action of Nordhausen sulphuric acid or sulphuric anhydride in the cold, acetoethylthiënonesulphonic acid is also formed, and can be obtained almost exclusively by careful working at 0°. The investigation of this acid is still in progress; its phenylhydrazine compound forms nearly colourless needles.

Thiënyl hexyl ketone, $C_4SH_3{\cdot}CO{\cdot}C_6H_{13}$, is prepared by adding aluminium chloride to a solution of thiophen and œnanthylic chloride in light petroleum, and decomposing the product of the reaction with water. It is a clear yellow oil of aromatic odour, and boils at 304°. *Thiënyl hexyl acetoxime*, $C_4SH_2{\cdot}C(NOH){\cdot}C_6H_{13}$, is crystalline, and melts at 49°. When oxidised with an alkaline solution of permanganate, the ketone yields caproic and β-thiophenic acids; it is therefore a β-derivative of thiophen. When heated with concentrated sulphuric acid, it is converted into œnanthylic and β-thiophensulphonic acids.

Ethylthiënyl hexyl ketone, $C_4SH_2Et{\cdot}CO{\cdot}C_6H_{13}$ [2 : 5], prepared in like manner from ethylthiophen, is a clear yellow oil of aromatic odour, boiling at 329—330°; it yields caproic and 2 : 5 thiophendicarboxylic acids when oxidised, and when heated with sulphuric acid is converted into œnanthylic and ethylthiophen-sulphonic and -disulphonic acids. The corresponding *acetoxime* melts at 38—39°, and does not crystallise.

A. J. G.

Isomeric Thiotolenic Acids. By S. Levi (*Ber.*, **19**, 656—659).—*β-Thiotolenic acid.*—By the action of sodium amalgam on a mixture of iodo-β-thiotolen and ethyl chlorocarbonate, ethyl-β-thiotolenate is obtained, which on hydrolysis with alcoholic potash, &c., is converted into the free acid. This crystallises in long needles, melts at 137°, and is most probably identical with the 2 : 5 methylthiophenic acid obtained by Paal (Abstr., 1885, 1206). When oxidised with

potassium permanganate in alkaline solution, it is converted into 2 : 5 thiophendicarboxylic acid. The calcium salt crystallises with $3\frac{1}{4}$ mols. H_2O.

γ-Thiotolenic acid, $C_4SH_2Me{\cdot}COOH$, prepared in manner similar from iodo-γ-thiotolen, is identical with an acid obtained by Demuth from γ-methylacetothiënone (this vol., p. 538). The *chloride*, $C_4SH_2Me{\cdot}COCl$, is a colourless liquid, boiling at 218—220°. The *amide*,

$$C_4SH_2Me{\cdot}CONH_2,$$

crystallises in long needles, and melts at 122—123°. A. J. G.

Croconic and Leuconic Acids. By R. Nietzki and F. Benckiser (*Ber.*, **19**, 772—778; comp. this vol., p. 449).—*Aniline croconate*, $C_5H_2O_5(NH_2Ph)_2$, is obtained by treating croconic acid dissolved in alcohol with aniline. When heated with alcohol on a water-bath, the solution becomes red, and after some time solidifies suddenly to a mass of slender, red needles. The new compound is a *dianilide* of *croconic acid*, of the formula $C_5(OH)_2O(NPh)_2$; it is sparingly soluble in the usual solvents except aniline, and does not melt without decomposition. It dissolves in alkalis, and is precipitated, partly unchanged, by acids. Hot alkalis decompose it into croconic acid and aniline. Aqueous ammonia converts it into *croconamic acid*, $NH_2{\cdot}C_5O_3{\cdot}OH$, or $NH : C_5O_2(OH)_2$. The *ammonium salt* forms red prisms; the *barium* (with 2 mols. H_2O) and *silver salts* are also described. The *phenylhydrazine compound*, $NHPh{\cdot}N : C_5O_2(OH)_2$, crystallises from alcohol in groups of needles which melt above 300°. The *potassium salt*, $C_{11}H_3N_2O_4K_2$, forms almost black needles, with a coppery lustre, readily soluble in water.

Croconic acid reacts readily with orthotoluylenediamine, with formation of a *compound*, $C_7H_6{<}\begin{smallmatrix}N\\N\end{smallmatrix}{>}C_5O(OH)_2$. The latter forms slender needles soluble in alcohol, insoluble in water. The *potassium salt*, $C_{12}H_6N_2O_2K_2$, crystallises in black needles with a metallic lustre.

Leuconditolylenequinoxaline, $C_7H_6{<}\begin{smallmatrix}N:C{\cdot}CO{\cdot}C:N\\ |\quad\quad |\\ N:C\text{——}C:N\end{smallmatrix}{>}C_7H_6$, is obtained by the action of leuconic acid (1 mol.) on toluylenediamine hydrochloride (2 mols.). It is insoluble in water, sparingly soluble in alcohol and glacial acetic acid, but dissolves readily in chloroform, from which it separates in gold-coloured needles containing about 20 per cent. of chloroform; this it loses at 140°. It melts above 300°, and can be sublimed partly without decomposition. It has feeble basic properties. The formation of this compound is fresh evidence in favour of the view previously brought forward by the authors, that anhydrous leuconic acid has the formula C_5O_5. The *phenylhydrazide*, $C_{25}H_{18}N_6$, crystallises from glacial acetic acid in splendid, cinnabar-red needles sparingly soluble in alcohol, readily soluble in chloroform. N. H. M.

Octylbenzene. By E. A. v. Schweinitz (*Ber.*, **19**, 640—643).—*Octylbenzene*, $C_6H_5{\cdot}C_8H_{17}$, is prepared by the action of sodium on a

mixture of bromobenzene and normal octyl bromide in ethereal solution. It is a colourless oil of sweet odour and taste, boils at 261—263° (uncorr.), does not solidify at 0°, and has a sp. gr. = 0·849 at 15° (water at 15° = 1). When oxidised, it yields a small quantity of benzoic acid. *Bromoctylbenzene*, $C_6H_4Br{\cdot}C_8H_{17}$, prepared by heating the hydrocarbon with bromine-water, is a clear yellow oil, boils at 285—290°, does not solidify at 0°, and is readily soluble in ether.

Octylbenzenesulphonic acid was obtained as a thick, syrupy liquid of strongly-pronounced acid properties by the action of Nordhausen sulphuric acid on the hydrocarbon. The silver salt, $C_8H_{17}{\cdot}C_6H_4{\cdot}SO_3Ag + H_2O$, the barium salt, $(C_{14}H_{21}SO_3)_2Ba + H_2O$, and the lead salt, $(C_{14}H_{21}SO_3)_2Pb + 3H_2O$, are described. A. J. G.

Action of Sodium on Bromo-derivatives of Benzene. By G. Goldschmiedt (*Monatsh. Chem.*, **7**, 40—47).—Paradibromobenzene was dissolved in pure dry ether, and the solution warmed on a water-bath with excess of sodium until all action ceased; diphenyl, paradiphenylbenzene, and a small quantity of benzene, were isolated from the ethereal solution. The greater part of the product of the action is insoluble in ether; after purification by solution in benzene and precipitation with alcohol, it forms a bright yellow, amorphous powder, agreeing in its properties with the substance described by Riese (this Journ., 1873, 62). On analysis, it gives numbers corresponding with the formula $C_{48}H_{32}Br_2$. The author regards it as a chain of eight phenylene-groups joined together in para-positions, and containing also two bromine-atoms in para-positions. The substance begins to soften at 220°, becomes darker on further heating, and finally melts completely at 265°. It is insoluble in ether and alcohol, easily soluble in benzene, chloroform, and carbon bisulphide. In order to ascertain if the limit of combination of the phenylene-groups had been reached, the experiment was repeated, and carried on for a much longer time. A substance was thus obtained possessing the same properties as the foregoing, which gave numbers on analysis agreeing with the formula $C_{78}H_{52}Br_2$, and may be regarded as consisting of 13 phenylene-groups with two bromine-atoms. The substance softens at 245°, and melts at 300°.

Pure metadibromobenzene, when treated in the same way as the para-compound, gave similar compounds. The portion insoluble in ether, purified as above, gave numbers agreeing with the formula $C_{48}H_{32}Br_2$. It is a yellow, amorphous powder, corresponding in properties with the para-derivative; it softens at 160°, and melts at 220°. A substance, $C_{78}H_{52}Br_2$, was also obtained on prolonged heating, which corresponds with the para-derivative; it softens at 200°, and melts at 250°.

Tribrombenzene, (1 : 3 : 5), remains unchanged after heating with sodium in ethereal solution for 55 hours. G. H. M.

Oxidation of Cymene. So-called Nitrocymene. By O. Widman and J. A. Bladin (*Ber.*, **19**, 583—589).—When a concentrated solution of potassium permanganate is added to 1 part of cymene

mixed with 10 parts of caustic soda solution (sp. gr. = 1·25), and the whole heated for some time on a water-bath. hydroxypropylbenzoic acid having all the properties ascribed to it by R. Meyer (Abstr., 1879, 157, 465, 795) together with a small quantity of terephthalic acid are formed. On the other hand, it has been already shown that when cymene is oxidised with nitric or chromic acids, the propyl-group is first attacked.

According to Fittica (this Journ., 1874, p. 684), nitric acid acts on cymene with formation of a liquid nitrocymene, $C_6H_3MePr{\cdot}NO_2$, and a solid nitrocymene (m. p. 125°); the same compounds were obtained by Landolph from camphor-cymene (this Journ., 1873, 1227). The authors repeated Fittica's experiments, and found that that portion of the product which distils with steam, consists chiefly of tolyl methyl ketone, already obtained by Michaelis (Abstr., 1882, 970), and by Claus (this vol., p. 462); a trace of what is probably a nitro-derivative is also formed. *Methyltolylacetoxime*, $OH{\cdot}N : CMe{\cdot}C_7H_7$, is prepared by the action of free hydroxylamine on the ketone; it forms short, lustrous crystals melting at 88°, almost insoluble in boiling water, readily soluble in alcohol. The *phenylhydrazine compound* crystallises in lustrous, colourless prisms which melt at 97°.

v. Gerichten has shown (Abstr., 1878, 787) that the substance described as "solid nitrocymene" (*loc. cit.*) is not nitrocymene.

When cymene is slowly dropped into a well-cooled mixture of nitric and sulphuric acids, a part remains unchanged, whilst a part is nitrated; a pure mononitrocymene could not be obtained.

N. H. M.

Oxidation of Homologues of Phenol. By B. Heymann and W. Koenigs (*Ber.*, **19**, 704—706).—The direct conversion of the homologues of phenol into the corresponding hydroxycarboxylic acids has so far only been effected by fusion with potash. Less directly it has been effected by converting the phenols into their alkyl ethers, oxidising, and then eliminating the alkyl-group by boiling with hydrochloric acid. The authors now show that the oxidation can be readily effected if the phenols are first converted into the corresponding double sulphates with potassium (best effected by adding potassium pyrosulphate to the phenols in alkaline solution at 60—70°), then oxidised with alkaline solution of potassium permanganate, and finally gently heated with hydrochloric acid on the water-bath. By this method, ortho- and para-cresol have been easily converted into the corresponding hydroxybenzoic acids.

A. J. G.

Phenyl Mesitylenyl Carbinol and its Derivatives. By E. Louïse (*Bull. Soc. Chim.*, **45**, 231—235).—By acting on a cold solution of monobenzoylmesitylene in aqueous alcohol with sodium amalgam, the author has obtained *phenyl mesitylenyl carbinol*, $C_6H_2Me_3{\cdot}CHPh{\cdot}OH$. This substance distils at about 300° to a viscid mass, which only becomes solid (even when crystals are added) after remaining for months. The crystals then obtained are long prisms which melt at 34°. It is insoluble in water, easily soluble in alcohol, ether, acetic acid, chloroform, &c., and can only be recovered from these solutions in the viscid state. The *ether*, $C_6H_2Me_3{\cdot}CHPh{\cdot}O{\cdot}CHPh{\cdot}C_6H_2Me_3$, was

obtained by boiling the alcohol with dilute sulphuric acid (1 part water to 1 part acid). It forms colourless crystals melting at 137°, soluble in ether, acetone, light petroleum, and chloroform, sparingly so in alcohol. The *ethyl ether*, $C_6H_2Me_3{\cdot}CHPh{\cdot}OEt$, can be obtained by adding a small quantity of strong sulphuric acid to an alcoholic solution of the carbinol and boiling the mixture. It crystallises in colourless prisms melting at 32°, and is soluble in alcohol and ether. The *acetate*, $C_6H_2Me_3{\cdot}CHPh{\cdot}OAc$, was prepared by digesting the carbinol with acetic anhydride. It crystallises in transparent prisms melting at 52°, and is soluble in alcohol. The *benzoate*, $C_{16}H_{17}{\cdot}OBz$, was obtained by heating the carbinol with benzoic acid. It forms colourless crystals melting at 94°, and is soluble in alcohol.

L. T. T.

Crystallographic Investigations. By T. Liweh (*Zeit. Kryst. Min.*, **11**, 246—250).—1. Paradichloroparadibromoquinone (Abstr., 1885, 1210), monosymmetric; $a : b : c = 1{\cdot}446 : 1 : 2{\cdot}850$; $\beta = 77° 30'$. 2. Paradichloroparadibromoquinol (Abstr., 1885, 1210), monosymmetric; $a : b : c = 2{\cdot}971 : 1 : 2{\cdot}723$; $\beta = 77° 24'$. 3. Terebilic acid (Abstr., 1885, 394), rhombic; $a : b : c = 0{\cdot}8093 : 1 : 0{\cdot}8576$. 4. Chloroterebic acid (Abstr., 1885, 393), rhombic; $a : b : c = 0{\cdot}9827 : 1 : 0{\cdot}7137$. 5. β-Naphthol; the author's crystallographic examination of this substance confirms Groth's results (*Annalen*, **152**, 285).

B. H. B.

Nitration of Dimethylaniline. By E. Nölting (*Ber.*, **19**, 545).—The author has repeated his experiments on the nitration of dimethylaniline, and finds, as stated by Groll (this vol., p. 347), that the main product is the metanitro-compound.

Mono- and Di-alkyl Derivatives of Metadiamines. By E. Nölting and T. Stricker (*Ber.*, **19**, 546—551).—*Ethylmetanitraniline*, $NO_2{\cdot}C_6H_4{\cdot}NHEt$, is obtained by heating 16 grams of metanitraniline, 14 grams of ethyl bromide, and 25 grams of 20 per cent. caustic soda solution for 12 hours at 100—110°. The product is dissolved in hydrochloric acid, treated with sodium nitrite and the *nitrosamine*, $NO_2{\cdot}C_6H_4{\cdot}NEt{\cdot}NO$, so obtained crystallised from alcohol, from which it separates in needles melting at 47°. This is then boiled with hydrochloric acid in alcoholic solution, treated with alkali, and the ethylnitraniline thus liberated purified by crystallisation from alcohol. It forms reddish-yellow needles, melts at 59—60°, dissolves readily in alcohol, ether, and light petroleum, and distils easily with steam. It can also be obtained together with the para-compound by nitrating ethylaniline. *Ethylmetaphenylenediamine*, $NH_2{\cdot}C_6H_4{\cdot}NHEt$, forms a yellowish oil boiling at 276° (uncorr.) which soon becomes brown when exposed to air. The *hydrochloride* was prepared.

Ethylchrysoïdine, $PhN_2{\cdot}C_6H_3(NH_2){\cdot}NHEt$, is prepared by adding diazobenzene chloride to a solution of ethylphenylenediamine hydrochloride. It crystallises from absolute alcohol in reddish-brown needles which reflect violet-blue light, and is soluble in water and

alcohol. The *platinochloride*, $(C_{14}N_4H_{16})_2,H_2PtCl_6$, forms a brick-red flaky precipitate insoluble in water. Ethylchrysoïdine dyes silk and cotton-wool mordanted with tannin of a redder shade than does ordinary chrysoïdine. *Ethylphenylene-blue*, analogous to Witt's toluylene-blue, is obtained by slightly warming 9 grams of nitrosodimethylaniline hydrochloride with 10 grams of ethylphenylenediamine hydrochloride and some sodium acetate. The blue dye is precipitated by common salt.

Methylmetanitraniline, $NO_2{\cdot}C_6H_4{\cdot}NHMe$, is obtained by heating 30 grams of metanitraniline, 31 grams ethyl iodide, and 8·7 grams caustic soda dissolved in alcohol for some hours, and then decomposing the nitrosamine formed with hydrochloric acid. It crystallises in reddish-yellow needles, readily soluble in alcohol and ether, and melts at 65—66°. *Methylmetanitrophenylnitrosamine*, $NO_2{\cdot}C_6H_4{\cdot}NMeNO$, is a yellow crystalline substance melting at 68—70° and readily soluble in alcohol. *Methylmetaphenylenediamine* is a yellowish oil boiling at 265—270° (uncorr.) which quickly resinifies when exposed to air.

Methylchrysoïdine, $PhN_2{\cdot}C_6H_3(NH_2){\cdot}NHMe$, is prepared in a manner similar to the ethyl-compound, and forms reddish-yellow flakes. *Ethylmetanitroparatoluidine*, $NO_2{\cdot}C_6H_3Me{\cdot}NHEt$ [NHEt : NO_2 : Me = 1 : 3 : 4], is obtained by nitrating monethylparatoluidine dissolved in 20 parts of sulphuric acid. It crystallises in long, flat, red prisms, readily soluble in alcohol and ether, and melts at 47—48°. *Ethylmetatoluylenediamine*, $NH_2{\cdot}C_6H_3Me{\cdot}NHEt$, is a yellowish liquid boiling at 280—283° (uncorr.). It gives all the characteristic reactions of metadiamines.

Diethylmetanitraniline is obtained by heating 20 grams of metanitraniline, 46 grams of ethyl iodide, and 12 grams of caustic soda dissolved in alcohol in a champagne bottle for 8 hours at 100°. The product is purified by converting it by means of acetic anhydride into nitrethylacetanilide, which is then saponified. It was also obtained together with the para-derivative by nitrating diethylaniline: the results of the reaction agree with those obtained by Groll (this vol., p. 347).

N. H. M.

Anhydro-compounds. By S. Niementowski (*Ber.*, **19**, 715—724). —In the formation of anhydro-compounds from the acetyl or benzoyl derivatives of ortho-diamines, it has never yet been shown whether the oxygen-atom of the acid radicle removes both hydrogen-atoms from one amido-group or from different amido-groups. The compound chosen to investigate this question was diamidoacetotoluide of the constitution I, which on the first assumption would yield an anhydro-compound of the constitution II, or on the second assumption, of the constitution III. By the continued action of acetic anhydride on the anhydro-compound, if the constitution II is correct, a diethenyl-

I.	II.	III.	IV.
(3.) ·NH_2	(3.) · N$\rangle$CMe	(3.) ·NH$\rangle$CMe	(3.) ·N$\rangle$CMe
(4.) ·NH·COMe	(4.) ·NH$\rangle$CMe	(4.) · N$\rangle$CMe	(4.) ·N$\rangle$CMe
(5.) ·NH_2	(5.) ·NH_2	(5.) ·NH_2	(5.) ·N$\rangle$CMe

triamidotoluene of the constitution IV should be formed, whilst the formation of such a compound from a substance of the constitu-

tion III would be inexplicable unless intermolecular change took place. The experimental results render it probable that III represents the constitution of the anhydro-compound.

Diamidoacetotoluide, $C_6H_2Me(NH_2)_2{\cdot}NHAc$, is prepared by reducing 3 : 5 dinitroparacetotoluide (Beilstein and Kuhlberg, *Annalen*, **158**, 341) with tin and hydrochloric acid, &c. It crystallises in nacreous prisms, does not show a sharp melting point, but blackens at 250°, and melts with decomposition at 262—264°; it is insoluble in benzene and ether, nearly insoluble in water, sparingly soluble in boiling acetone, soluble in boiling alcohol and in glacial acetic acid. The *hydrochloride*, $C_9H_{13}N_3O,HCl + \frac{1}{2}H_2O$, crystallises in thick, concentrically grouped needles.

Ethenyltriamidotoluene, $NH_2{\cdot}C_6H_2Me : N_2H : CMe$, is obtained as hydrochloride by long-continued boiling of the preceding substance with hydrochloric acid. It crystallises with 1 mol. H_2O in monoclinic tables; $a : b : c = 1{\cdot}5813 : 1 : 0{\cdot}8216$; $\beta = 82° 44'$; melts at 100°, and is readily soluble in alcohol and boiling water, sparingly soluble in ether and benzene. The hydrochloride crystallises in rhombic tables.

Acetylethenyltriamidotoluene is obtained by heating the preceding compound with acetic chloride or anhydride, or more readily by boiling diamidoacetotoluide with acetic anhydride for five minutes. It crystallises with $1\frac{1}{2}$ mol. of acetic acid in concentrically grouped, satiny, white needles, and melts at 166°; the acetic acid cannot be removed without decomposition occurring. When boiled with hydrochloric acid, it yields ethenyltriamidotoluene hydrochloride.

Nitroethenyltoluylenediamine, $NO_2{\cdot}C_6H_2Ne : N_2H : CMe$, is prepared by nitrating ethenyltoluylenediamine; it crystallises in tufts of needles, melts at 201—202°, and is readily soluble in the ordinary solvents.

A. J. G.

Azo- and Diazo-compounds of Thymol. By Mazzari and Possetto (*Chem. Centr.*, 1886, 136).—An alkaline thymol solution, when added to diazobenzene chloride, produces a dark-brown precipitate partly soluble in warm potash solution. The soluble portion is reprecipitated by addition of acetic acid; it melts at 85—90°, and has the composition $OH{\cdot}C_6H_2MePr{\cdot}N_2Ph$. The insoluble portion melts at 168°, and is the corresponding diazo-compound. H. B.

Action of Benzaldehyde on Hydrazobenzene. By P. T. Clève (*Bull. Soc. Chim.*, **45**, 188).—When hydrazobenzene is heated with benzaldehyde in a reflux apparatus, azobenzene is formed, the hydrazobenzene seeming to act as a reducing agent; by adding zinc chloride to the mixture and heating, a lively reaction takes place, the benzylidene-benzidene described by Schiff being formed. A. P.

Phenylhydrazine Compounds. By M. Pickel (*Annalen*, **232**, 228—235).—The preparation of benzophenonephenylhydrazine has been described by E. Fischer (Abstr., 1884, 1151). The compound melts at 137°. It is insoluble in water, and sparingly soluble in cold alcohol. When boiled with hydrochloric acid, it is partially decomposed into phenylhydrazine and benzophenone. *Benzoinphenylhydrazine*, prepared by heating benzoin with excess of phenylhydrazine and a

small quantity of alcohol, forms colourless needles. It melts at 155°, and is freely soluble in alcohol, ether, benzene, and chloroform. *Benzilphenylhydrazine*, $N_2HPh:CPh\cdot CPh:N_2HPh$, melts at 225°, and dissolves in warm chloroform and benzene. *Glyoxaldiphenylhydrazine*, $N_2HPh:CH\cdot CH:N_2HPh$, is formed on warming an aqueous solution of sodium acetate, phenylhydrazine hydrochloride, and glyoxal. The compound melts at 169—170°, and dissolves freely in warm alcohol, benzene, and chloroform. Strong hydrochloric acid precipitates reddish-yellow crystals of the hydrochloride, $C_{14}H_{14}N_4,HCl$, from the alcoholic solution. The salt melts at 155—156°, and is resolved into its components by water. The nitrobenzaldehydes unite with phenylhydrazine, forming crystalline compounds of a beautiful red colour. The ortho-compound melts at 153°, the meta- at 121°, and the para- at 155°. Phthalylphenylhydrazine has been recently described by Hötte (this vol., p. 353). W. C. W.

Reduction of Hydrobenzamide. By O. Fischer (*Ber.*, **19**, 748—749).—If an alcoholic solution of hydrobenzamide is treated with 3 per cent. sodium amalgam, it is converted into a secondary base, most probably *benzylidinedibenzylimide*, $CHPh(NH\cdot CH_2Ph)_2$; this substance is also formed by the action of sodium on solutions which are not too concentrated or too hot. By more energetic reduction with excess of sodium and with aid of heat, hydrobenzamide or its first reduction product is converted into toluene and benzylamine.

Benzylidineaniline when similarly treated is converted into benzylaniline. A. J. G.

Nitro-derivatives of Substituted Benzamide. By P. v. Romburgh (*Rec. Trav. Chim.*, **4**, 384—392).—The alcoholic derivatives of benzamide, when treated with absolute nitric acid, yield nitro-compounds in which the hydrogen of the benzene nucleus is replaced. Thus dimethylbenzamide, under these conditions, gives a *nitro-derivative*, $NO_2\cdot C_6H_4\cdot CONMe_2$, which forms white crystals, melting at 57°; similarly diethylbenzamide yields a mono-nitro-derivative, $NO_2\cdot C_6H_4\cdot CONEt_2$; methylbenzamide, a derivative,

$$NO_2\cdot C_6H_4\cdot CONHMe,$$

which crystallises in white needles, melting at 170°. But benzamide, when heated with absolute nitric acid, yields mononitrobenzoic acid with evolution of nitrous oxide; in this respect it resembles the paraffinoïd amides. V. H. V.

Methylphenazine. By V. Merz and A. Ris (*Ber.*, **19**, 725—728).—*Methylphenazine*, $C_6H_4\langle\begin{smallmatrix}N\\|\\N\end{smallmatrix}\rangle C_6H_3Me$, is obtained by heating catechol with orthotoluylenediamine in equimolecular proportions at 200—220° for about 50 hours. It crystallises in clear yellow needles, melts at 117°, can be sublimed or distilled with steam, and distils alone at about 350°, but not without decomposition. It is sparingly soluble in light petroleum or boiling water, readily in most other solvents, has

basic properties, dissolves with yellow colour in dilute acids, and gives a blood-red coloration with concentrated sulphuric acid. The *platinochloride*, $(C_{13}H_{10}N_2)_2,H_2PtCl_6 + 6H_2O$, crystallises in yellow plates. The *picrate* melts at 168°. When methylphenazine in alcoholic ammoniacal solution is treated with hydrogen sulphide, it yields silvery white plates seemingly of a hydro-compound.

A. J. G.

Action of Ammonia on Terephthalaldehyde. By H. Oppenheimer (*Ber.*, **19**, 574—577).—*Hydrobenzamidetrialdehyde*,

$$N_2(CH\cdot C_6H_4\cdot CHO)_3,$$

is obtained by treating finely powdered terephthalaldehyde with strong aqueous ammonia. The reaction begins in a short time, and is accompanied with a rise of temperature which should be kept down by cooling. The whole is frequently shaken and allowed to remain for 6 to 8 days until no further precipitation occurs. It is a soft, white powder consisting of small, matted needles almost insoluble in water, alcohol, and ether. Dilute acids decompose it into terephthalaldehyde and the ammonium salt of the acid employed. A sulphur-coloured *phenylhydrazine-derivative* was prepared. When oxidised with potassium permanganate, it yields *hydrobenzamidotricarboxylic acid* crystallising in lustrous, rhombohedral plates.

Xylidinediamine, $C_6H_4(CH : NH)_2$ [= 1 : 4], is prepared by passing dry ammonia into an alcoholic solution of terephthalaldehyde; it separates in very brittle, glassy crystals. Boiling water and acids decompose it into its original constituents. It is also formed by the action of dry ammonia on powdered terephthalaldehyde; water is formed in the reaction.

N. H. M.

Action of Bromacetophenone on Phenylhydrazine. By O. Hess (*Annalen*, **232**, 234—235).—A compound of the composition $N_2Ph : C_2H_2Ph$ is obtained on mixing alcoholic solutions of bromacetophenone and phenylhydrazine. It crystallises in yellow, glistening needles, and melts at 137°. It dissolves freely in ether, chloroform, carbon bisulphide, ethyl acetate, boiling alcohol, and light petroleum. It is decomposed by mineral acids.

W. C. W.

Condensation of Hippuric Acid with Aldehydes. By O. Rebuffat (*Gazzetta*, **15**, 527—531).—When hippuric acid or its sodium salt is heated with salicylic aldehyde in presence of acetic anhydride, a substance, $C_{16}H_{13}O_4N$, is produced, crystallising in yellow prisms which melt at 135—136°. But this on treatment with various solvents, such as alcohol or benzene, is transformed into benzoylimidocoumarin melting at 171°, the product of the above reaction observed by Plöchl (Abstr., 1884, 604), and of composition identical with the above. It behaves like a coumarin, being converted by the action of alkalis into an acid melting at 185° with decomposition. It is suggested as the more probable of alternative hypotheses, that the immediate product of the above reaction has the composition

$$OH\cdot CH<\begin{matrix}CH(NHBz)\\ C_6H_4\text{——}O\end{matrix}>CO,$$

whilst to the acid obtained from it is assigned the formula $OH{\cdot}C_6H_4{\cdot}CH:C(NHBz){\cdot}COOH$. V. H. V.

Derivatives of Amidobenzoic Acid. By G. Pellizzari (*Gazzetta*, **15**, 555—572, and *Annalen*, **232**, 145—168).—Derivatives of 1 : 3 amidobenzoic acid, in which a hydrogen-atom in the amido-grouping is replaced by a monobasic acidic radicle, are prepared from amidobenzoic acid with either the ethyl salt of the monobasic acid or preferably its amide, thus: $C_nH_m{\cdot}CONH_2 + NH_2{\cdot}C_6H_4{\cdot}COOH = C_nH_m{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}COOH + NH_3$. In some cases, it is merely necessary to fuse the two acids together.

Formamidobenzoic acid, $CHO{\cdot}NH{\cdot}C_6H_4{\cdot}COOH$, crystallises in minute needles, melting at 225° with decomposition, thus:

$$COH{\cdot}NH{\cdot}C_6H_4{\cdot}COOH = C_6H_4{<}\begin{matrix}NH\\CO\end{matrix}{>} + H{\cdot}COOH;$$

it is sparingly soluble in cold, readily in hot water.

Acetamidobenzoic acid, prepared by the above process, agrees in properties, except melting point (240—241°), with the acid described by Foster (melting point 220—230°) (*Bull. Soc. Chim.*, 1860, 213).

Butyramidobenzoic acid, $CPrO{\cdot}NH{\cdot}C_6H_4{\cdot}COOH$, crystallises in needles melting at 208—209°; it is decomposed by acids and alkalis into its constituents.

Œnanthamidobenzoic acid, $C_7H_{13}O{\cdot}NH{\cdot}C_6H_4{\cdot}COOH$, crystallises in needles melting at 202°, sparingly soluble in boiling water, moderately soluble in ether and alcohol; its salts are readily soluble.

Benzamidobenzoic acid, $NHBz{\cdot}C_6H_4{\cdot}COOH$.—On heating ethyl benzoate with amidobenzoic acid, two products are obtained—one soluble the other insoluble in alcohol. The former is the above acid, which crystallises in minute prisms melting at 248°, and is very soluble in alcohol, sparingly soluble in water and ether; its *barium* salt forms white crystalline crusts. The substance insoluble in alcohol, mistaken by Foster for the acid, is probably an *anhydride of benzoyltribenzamic acid*, $NHBz{\cdot}C_6H_4{\cdot}CONH{\cdot}C_6H_4{\cdot}CONH{\cdot}C_6H_4{\cdot}COOH$.

Benzamidobenzanilide, $NHBz{\cdot}C_6H_4{\cdot}CONHPh$, obtained from the above acid and aniline, crystallises in glistening leaflets melting at 225°.

Glycollamidobenzoic acid, $OH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}COOH$, crystallises in glistening needles, melting at 212°, sparingly soluble in cold, readily in hot water; its *acetyl*-derivative crystallises in white leaflets, melting at 198°, soluble in alcohol and ether. The acid when heated at 220° loses a molecule of water, and is converted into an anhydride, $<\begin{matrix}CH_2\\CO\end{matrix}{>}N{\cdot}C_6H_4{\cdot}COOH$, a yellow crystalline powder melting at 246—248°.

Lactamidobenzoic acid, $OH{\cdot}CHMe{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}COOH$, crystallises in minute prisms which melt at 161—162°; its *acetyl*-derivative forms crystalline crusts; its anhydride, obtained in the course of the preparation of the acid, is a crystalline powder melting at 243°.

Salicamidobenzoic acid, $OH{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}COOH$, is a crystalline powder not showing a definite point of fusion owing to its

decomposition with evolution of carbonic anhydride and phenol; it gives a violet coloration with ferric chloride. V. H. V.

Oxalamidobenzoic Acids. By H. Schiff (*Gazzetta*, **15**, 534—547, and *Annalen*, **232**, 129—145).—*Ethyloxalamidobenzoic acid*, $OEt{\cdot}C_2O_2{\cdot}NH{\cdot}C_6H_4{\cdot}COOH$, obtained by heating amidobenzoic acid with ethyl oxalate and alcohol, forms colourless, silky needles melting at 225°, and transformed at that temperature into ethyl oxalate and oxalodibenzamic acid. On treatment with ammonia, it yields the ammonium salt of amidoxalobenzamic acid, from which the acid $NH_2{\cdot}C_2O_2{\cdot}NH{\cdot}C_6H_4{\cdot}COOH$ is obtained. This substance crystallises in small scales resembling oxamide; when heated at 160—170° it is converted into oxamide and oxalodibenzamic acid; its *phenyl*-derivative, $NHPh{\cdot}C_2O_2{\cdot}NH{\cdot}C_6H_4{\cdot}COOH$, crystallises in glistening plates which melt at 300—305°.

Ethyloxalamidobenzamide, $OEt{\cdot}C_2O_2{\cdot}NH{\cdot}C_6H_4{\cdot}CONH_2$, prepared by heating a solution of amidobenzamide in ethyl oxalate, forms spherical aggregates of glistening needles, melting at 191·5°, soluble in alcohol. A few degrees above its point of fusion, it is transformed into ethyl oxalate and oxalodibenzamidodiamide. Its *phenyl*-derivative, $OEt{\cdot}C_2O_2{\cdot}NH{\cdot}C_6H_4{\cdot}CONHPh$, obtained from amidobenzanilide and ethyl oxalate, crystallises in silky needles melting at 180°.

Oxalodibenzamic acid, $C_2O_2(NH{\cdot}C_6H_4{\cdot}COOH)_2$, best prepared by heating ethyloxalamidobenzoic acid with a slight excess of amidobenzoic acid, is insoluble in water and alcohol, soluble in concentrated acids. Its *amic acid*, obtained together with its amide by heating equimolecular proportions of ethyloxalamidobenzoic acid and amidobenzamide, is a rose-red substance, infusible, insoluble in boiling water, sparingly soluble in alcohol.

The *amide*, $C_2O_2(NH{\cdot}C_6H_4{\cdot}CONH_2)_2$, similarly prepared, is a white crystalline powder insoluble in water and alcohol.

Oxalamidobenzoic acid, $OH{\cdot}C_2O_2{\cdot}C_6H_4{\cdot}COOH + H_2O$, prepared from amidobenzoic and oxalic acids, forms dendritic aggregates of small needles; its alkaline salts are very soluble; those of the heavy metals are sparingly soluble.

Malonamidobenzoic acid, obtained by a similar method, yields derivatives analogous to those described above; the *dibenzamic acid*, $CH_2(CO{\cdot}NH{\cdot}C_6H_4{\cdot}COOH)_2$, is a white, infusible, crystalline powder; *hydrogen ethyl malonamidobenzoate*, $COOEt{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}COOH$, forms long silky needles melting at 172—173°, and decomposes a few degrees above into ethyl malonate and malonodibenzamic acid.

V. H. V.

Phthalaldehydic Acid. By S. Racine (*Ber.*, **19**, 778—779).—*Monobromophthalide*, $C_6H_4{<}\overset{CHBr}{CO}{>}O$, is obtained by the action of bromine-vapour on phthalide at 130—150°. It crystallises in plates melting at 85—86°, and dissolves in ether, carbon bisulphide, and chloroform. When oxidised, it is converted into phthalic acid. Absolute alcohol acts on it with formation of an ether, $C_6H_4{<}\overset{CH(OEt)}{CO}{>}O$. *Phthalaldehydic acid*, $CHO{\cdot}C_6H_4{\cdot}COOH$, is

obtained by warming bromophthalide with water. It dissolves readily in water, alcohol, and ether, and melts at 98—100°. The *phenylhydrazine-derivative* was prepared. N. H. M.

Behaviour of Opianic and Nitropianic Acids towards Phenylhydrazine. By C. Liebermann (*Ber.*, **19**, 763—766).—*Opianylphenylhydrazide*, $C_6H_2(OMe)_2<\begin{matrix}CO\cdot NPh\\CH{=}N\end{matrix}>$, is obtained by mixing a hot, concentrated, aqueous solution of opianic acid with a hot aqueous solution of phenylhydrazine hydrochloride and sodium acetate (each 1 mol.). It crystallises from alcohol in almost colourless needles which melt at 175°. It is insoluble in alkalis, but dissolves in fuming hydrochloric acid. Sulphuric acid does not act on it at 130°.

Nitropianic acid phenylhydrazine, $C_{16}H_{15}N_3O_6$, is prepared in a similar manner to the above compound, and forms splendid carmine-red needles; it melts at 184°.

Nitropianylphenylhydrazide, $NO_2\cdot C_6H(OMe)_2<\begin{matrix}CO\cdot NPh\\CH{=}N\end{matrix}>$, is formed when the last-mentioned compound is boiled with glacial acetic acid or by adding water to a solution of the red phenylhydrazine compound in sulphuric acid. It crystallises in yellow needles having a silky lustre, and melts at 173°. It is soluble in hot fuming hydrochloric acid, and is precipitated on the addition of water.

Opianic acid reacts with hydroxylamine hydrochloride, also with elimination of 2 mols. of water. N. H. M.

The Re-formation of Ethyl Succinosuccinate from Ethyl Dihydroxyterephthalate. By F. Herrmann (*Ber.*, **19**, 702—704).—The author denies the accuracy of Baeyer's statement (this vol., p. 445) that ethyl dihydroxyterephthalate is converted into ethyl succinosuccinate when boiled with zinc and hydrochloric acid in alcoholic solution; not even a trace of the succinosuccinate is formed.

A. J. G.

Quinonetetracarboxylic Acid. By J. U. Nef (*Ber.*, **19**, 516—520).—*Ethyl quinonetetracarboxylate*, $C_6O_2(COOEt)_4$, is prepared by gently heating ethyl azopyromellitate (this vol., p. 64) with nitric acid (1·4) on the water-bath; it crystallises in yellow needles, melts at 148—150°, sublimes readily, and is destitute of odour. It is soluble in hot alcohol or ether, and does not react with hydroxylamine.

Ethyl quinoltetracarboxylate, $C_6(OH)_2(COOH)_4$, is prepared by gently warming the above salt in acetic acid solution with zinc-dust. It crystallises in bright yellow needles having a bluish lustre, melts at 126—128°, can be sublimed by careful heating, and dissolves readily in alcohol, ether, and glacial acetic acid, the solutions showing a pure blue fluorescence; the alcoholic solution gives a bluish-green coloration. It dissolves in dilute aqueous soda with yellow colour, but with concentrated soda, a deep vermilion-coloured sodium salt separates; on heating, hydrolysis occurs.

When ethyl quinoltetracarboxylate in alcoholic solution is treated with zinc-dust and concentrated hydrochloric acid, a *tetrahydro*-deri-

vative, $C_6H_4O_2(COOEt)_4$, is formed. This crystallises in colourless needles or prisms, containing water of crystallisation, melts when anhydrous at 142—144°, and dissolves sparingly in alcohol, ether, and carbon bisulphide, the solutions showing a feeble blue fluorescene. The alcoholic solution gives a cherry-red coloration with ferric chloride. A. J. G.

Condensation Products from β-Anilido-acids. By A. Reissert and F. Tiemann (*Ber.*, **19**, 622—628; comp. Schiller-Wechsler, Abstr., 1885, 900).—*Pyranilpyroic acid*, $C_{10}H_{10}NO{\cdot}COOH$, is obtained by heating anilidopyrotartaric acid for some time a little above its melting point. It is a white, crystalline powder, melts at 165°, and is sparingly soluble in water, more readily in alcohol and ether. *Pyranilpyroic anhydride*, $C_{11}H_9NO_2$, is obtained by heating the acid more strongly; it crystallises in yellowish-white needles, melts at 98°, distils unchanged, is readily soluble in alcohol and ether, sparingly in water, and is readily reconverted into the acid when heated with aqueous acids.

When an aqueous solution of dibromosuccinic acid is boiled with aniline, there is formed, not dianilidosuccinic acid as might be expected, but a mixture of two crystalline substances which can be separated by their different solubility in water. The more soluble compound, $C_{16}H_{14}N_2O_3$, has marked acid properties, and melts at 175°; the more sparingly soluble substance, $C_{16}H_{12}N_2O_2$, shows very feeble acid properties, and melts at 231°. These substances must be regarded as derived from dianilidosuccinic acid by the elimination of 1 and 2 mols. H_2O respectively. Their constitution and that of the preceding substances is the subject of further investigation.

A. J. G.

Anhydrides of Aromatic Sulphonic Acids. By J. Rosenberg (*Ber.*, **19**, 652—655).—The author's observations having shown that polyhalogenated thiophens when treated with fused pyrosulphuric acid yield not sulphonic acids, but the corresponding anhydrides (Abstr., 1885, 1051, and this vol., p. 534), it seemed of interest to ascertain if a similar result would be obtained with analogous benzene-derivatives.

Paradibromobenzenesulphonic anhydride, $(C_6H_3Br_2{\cdot}SO_2)_2O$, is prepared by heating paradibromobenzene with pyrosulphuric acid on the water-bath. It forms an amorphous, white mass, which does not show a sharp melting point; it is very sparingly soluble in ether, alcohol, or benzene, even on boiling; and is with great difficulty converted into the corresponding acid by boiling water. When boiled with a mixture of phosphoric chloride and oxychloride, it is converted into a *chloride*, $C_6H_3Br_2{\cdot}SO_2Cl$, identical with that prepared by Hübner.

Tribromobenzenesulphonic anhydride, $(C_6H_2Br_3{\cdot}SO_2)_2O$, prepared in a similar manner from 1 : 2 : 4 tribromobenzene, is an amorphous substance closely resembling the dibromo-anhydride in properties. The *sulphochloride*, $C_6H_2Br_3{\cdot}SO_2Cl$, is crystalline and melts at 81°.

A. J. G.

Indole-derivatives. By S. Hegel (*Annalen*, **232**, 214—221).—Methylparatolylhydrazine unites with pyroracemic acid, forming a

compound, $C_{11}H_{14}N_2O_2$, which crystallises in yellow prisms. The crystals soften at 81°, and melt at 83·5° with decomposition. They are soluble in alcohol, ether, benzene, and chloroform. Methyltolylhydrazinepyroracemic acid is decomposed by digestion with 20 times its volume of 10 per cent. hydrochloric acid, yielding *methylparatolindolecarboxylic acid*, $C_{11}H_{11}NO_2$. The acid melts at 221°, with decomposition, yielding carbonic anhydride and methylparatolindole. It crystallises in white needles, and is dissolved by warm alcohol, chloroform, benzene, and warm glacial acetic acid. It also dissolves freely in alkalis, and is precipitated in the form of sodium salt on the addition of sodium hydroxide in excess.

Methylparatolindole is an oily liquid, boiling about 242—245°. It forms crystalline precipitates with picric and nitric acids.

A yellow crystalline precipitate is produced when sodium hypochlorite is added to a neutral solution of methyltolindolecarboxylic acid in sodium hydroxide. The precipitate melts at 135°. It is decomposed by boiling water, yielding methylpseudotolisatin, $C_{10}H_9NO_2$. This substance forms red needles, which melt at 148°.

Ethylparatolylhydrazinepyroracemic acid is deposited from its ethereal solution in needles. It is soluble in alcohol, ether, benzene, chloroform, and in warm light petroleum. It is best converted into *ethylparatolindolecarboxylic acid*, $C_{12}H_{13}NO_2$, by means of phosphoric acid. This acid melts at 202°, and splits up at a higher temperature into carbonic anhydride and ethylparatolindole. It is soluble in ether, benzene, chloroform, and acetic acid.

Ethylparatolindole, $C_{11}H_{13}N$, boils between 253° and 255°. The aqueous emulsion of the base gives a red coloration, followed by a red precipitate with fuming nitric acid. *Ethylpseudoparatolisatin*, $C_{11}H_{11}NO_2$, forms dark-red needles, melting at 109°. This compound has been recently described by Duisberg (Abstr., 1885, 543).

Methylorthotolindolecarboxylic acid, $C_{11}H_{11}NO_2$, prepared from crude methyltolylhydrazinepyroracemic acid, resembles the corresponding para-compound in many respects, but it melts at 209—210°, and is very soluble in cold alcohol. It is deposited from a solution in warm benzene in white needles, which turn pink on exposure to the air. At a temperature above its melting point it decomposes, forming methylorthotolindole.

Methylpseudorthotolisatin, $C_{10}H_9NO_2$, forms brick-red needles. It melts at 157°. W. C. W.

Condensation of Aromatic Bases with Aldehydes. By A. Kaeswurm (*Ber.*, **19**, 742—747).—This paper describes the preparation and properties of substituted benzaldehyde-greens containing halogens.

By the condensation of parachlorobenzaldehyde with dimethylaniline in the manner described by Fischer for the preparation of leucomalachite-green, a leuco-base of the formula

$$C_6H_4Cl\cdot CH(C_6H_4\cdot NMe_2)_2$$

is obtained. This crystallises in colourless, concentrically-grouped needles, melts at 142—143° with green coloration, is readily soluble

in benzene, less soluble in alcohol and ether, sparingly soluble in light petroleum, insoluble in water, and yields colourless salts with mineral acids, which are very soluble in water. The platinochloride, $C_{23}H_{25}N_2Cl,H_2PtCl_6$, forms pale-yellow crystals containing water. The colour-base, $C_{23}H_{25}N_2ClO$, prepared by oxidation of the leuco-base, forms colourless crystals, rapidly turning reddish-brown on exposure to air, melts at 144—146°, with intense green coloration, and is readily soluble in benzene and ether, insoluble in light petroleum; the zincochloride dyes fabrics a strong bluish-green tint.

The leuco-base, $C_{27}H_{33}N_2Cl$, obtained by the condensation of parachlorobenzaldehyde with diethylaniline, resembles that above described, but melts at 110°. When oxidised, it yields a colour-base, $C_{27}H_{33}ClN_2O$, which crystallises in large, lustrous, pale-rose coloured tables, and melts at 120—121°. The zincochloride dyes fabrics the same tint as that given by the methyl compound.

By the condensation of parachlorbenzaldehyde with diphenylamine, only an amorphous pale-red base was obtained, whose alcoholic solution gave a fine blue coloration when oxidised with chloranil. This base does not show the tinctorial properties of the non-chlorinated compound.

Paranitrotetrethyldiamidotriphenylmethane, $C_{27}H_{33}N_3O_2$, obtained by the condensation of paranitrobenzaldehyde with diethylaniline (comp. Fischer, Abstr., 1882, 392), crystallises in reddish-brown monoclinic tables, showing the faces ∞P, $\infty P\infty$, 0P, melts at 113°, is stable when exposed to air, and yields a yellowish-green dye on oxidation with chloranil. When reduced with zinc-dust and hydrochloric acid, it yields *tetrethylparaleucaniline*, $C_{27}H_{35}N_3$; this crystallises in nodules composed of slender, concentrically grouped needles, melts at 118°, and is very readily oxidised by exposure to air. The zincochloride of the oxidised base dyes fabrics a pure violet. The acetyl-derivative of the leuco-base when oxidised is converted into *paracetamidomalachite-green*, a green dye. A. J. G.

Derivatives of Triphenylamine. By C. Heydrich (*Ber.*, **19**, 758—761; comp. Abstr., 1885, 1213).—*Hexaphenylrosaniline*, $OH{\cdot}C(C_6H_4{\cdot}NPh_2)_3$, is prepared by heating triphenylamine with carbonyl chloride for four hours at 180—200°. The blue dye thus formed is extracted with ether, dissolved in acetone, and filtered; on evaporating the acetone, a brittle mass is obtained, consisting of hexaphenylrosaniline hydrochloride; the free base is obtained from this by adding ammonia to the alcoholic solution. The *hydrochloride* has a fine blue colour and a red metallic lustre. A solution of the base in sulphuric acid has a violet-blue colour, which changes to pure blue when alcohol is added. The *picrate* forms small, matted, greenish-yellow needles; the *platinochloride*, $2N(C_6H_4{\cdot}NH_2)_3,3H_2PtCl_6$, crystallises in small needles, soluble in much water and alcohol.

Hexamethyltriamidotriphenylamine methochloride,

$$N(C_6H_4{\cdot}NMe_2)_3,3MeCl,$$

is obtained by heating triamidotriphenylamine hydrochloride with an

excess of methyl alcohol for six hours at 180—200°. The *platinochloride*, $2N(C_6H_4{\cdot}NMe_2)_3,3Me_2PtCl_6$, forms a greenish powder.

A number of experiments are described, the results of which show that the triamidotriphenylamine previously described (*loc. cit.*) by the author is not identical with Nietzki's leucosaffranin (Abstr., 1883, 731).

N. H. M.

Isomeric α-Naphthylaminesulphonic Acids. By O. N. Witt (*Ber.*, **19**, 578—582; compare this vol., p. 364).—It was previously shown (*loc. cit.*) that sulphuric acid acts on α-naphthylamine with formation of an acid identical with Piria's naphthionic acid. When dry α-naphthylamine hydrochloride is added to fuming sulphuric acid (containing 25 per cent. of sulphuric anhydride), *α-naphthalidinesulphonic acid*, $C_{10}H_8N{\cdot}SO_3H$, is obtained. It forms nodular masses of microscopic needles, and is about four times as soluble in water as is naphthionic acid. The *sodium* (with 5 mols. H_2O), *calcium* (with 6 mols. H_2O), and *barium* (with 8 mols. H_2O) salts were prepared. The acid resembles in many respects Cleve's amidonaphthalenesulphonic acid, but differs considerably in the amount of water of crystallisation contained in the salts. The constitution of naphthionic acid is probably [$NH_2 : SO_3H = 1 : 4$], and that of Cleve's acid [$NH_2 : SO_3H = 1 : 4'$]. The author is endeavouring to determine the constitution of the new acid.

N. H. M.

Naphthylhydrazines. By E. Fischer (*Annalen*, **232**, 236—243).—*α-Naphthylhydrazine* is best prepared by adding the equivalent quantity of sodium nitrite to 50 grams of finely powdered naphthylamine, suspended in 400 grams of hydrochloric acid (sp. gr. 1·1). The dark-brown solution is filtered and added to 250 grams of stannous chloride, dissolved in cold hydrochloric acid. The mixture is now warmed until the greater part of the precipitate redissolves, and a nearly colourless solution is formed. On cooling, the hydrochloride of the hydrazine is deposited as a crystalline mass. The crude hydrazine, obtained by adding sodium hydroxide to a hot aqueous solution of the hydrochloride, is purified by recrystallisation from a mixture of alcohol and ether, and by rapid recrystallisation from boiling water. It is obtained perfectly colourless by distillation under reduced pressure. The base melts at 116—117° and boils at 203°, under a pressure of 20 mm. It oxidises on exposure to the air. It is sparingly soluble in ether, but dissolves freely in warm alcohol, chloroform, and benzene. The *hydrochloride*, $C_{10}H_{10}N_2,HCl$, crystallises in plates. It is freely soluble in water and sparingly soluble in hydrochloric acid. The neutral *sulphate* also crystallises in plates; it is sparingly soluble in hot water. The *nitrate* is soluble in water. The *acetate* is decomposed by water; sodium acetate precipitating the base from aqueous solutions of its salts. Dilute acetic acid, however, readily dissolves α-naphthylhydrazine in presence of grape-sugar. Naphthylhydrazine closely resembles phenylhydrazine in its properties and its reactions. *α-Naphthylhydrazinepyroracemic acid* is precipitated on the addition of pyroracemic acid to a solution of α-naphthylhydrazine or its salts. The compound is deposited from its solution in hot alcohol in needles. It is soluble in alkalis, and is

reprecipitated from these solutions by acids. The acid melts at 159° with decomposition.

α-Naphthylhydrazine unites with benzaldehyde and with acetone, forming crystalline compounds. The latter melts at 74°, and is decomposed at a higher temperature; it is freely soluble in alcohol, ether, acetone, and benzene, and in dilute acids. *Diazonaphthalenimide*, $C_{10}H_7{\cdot}N_3$, appears to be formed when sodium nitrite is added to a hydrochloric acid solution of naphthylhydrazine. It is insoluble in dilute acids and is decomposed by distillation.

β-Naphthylhydrazine melts at 124—125°, and dissolves freely in hot alcohol, benzene, and chloroform. It is more soluble in hot water, and oxidises less readily on exposure to the air than the α-compound. The hydrochloride and nitrate dissolve freely in hot water, but the sulphate is sparingly soluble. The acetate is decomposed by water. W. C. W.

α-Azoxynaphthalene-α-Sulphonic Acid. By J. E. Allen (*Bull. Soc. Chim.*, **45**, 184—185).—The potassium salt of *α-azoxynaphthalene-α-sulphonic acid*, $N_2O(C_{10}H_6{\cdot}SO_3K)_2 + H_2O$, may be obtained by heating 37 parts of α-nitronaphthalene-α-sulphonic acid (obtained by the action of sulphuric acid on mononitronaphthalene) with 50 parts of potash, dissolved in 95 per cent. alcohol; the brown product obtained is crystallised from boiling water; it forms rhombic tables, which lose their water of crystallisation at 170—180°. The *free acid*, obtained from the barium salt, is very soluble in water, forming a brownish-red solution; it dissolves in sulphuric acid with a violet colour. The *sodium salt*, $N_2O(C_{10}H_6{\cdot}SO_3Na)_2 + 2H_2O$, crystallises in tables; dried at 100°, it retains ½ mol. H_2O. The *barium*, *calcium*, and *lead* salts are also described. The potassium salt of the acid may also be obtained by heating the α-nitronaphthalene-α-sulphonic acid on the water-bath with zinc powder and excess of potash. A. P.

Action of Sulphuric Acid on β-Chloronaphthalene. By K. Arnell (*Bull. Soc. Chim.*, **45**, 184).—By heating β-chloronaphthalene at 130—140° with a mixture of concentrated and fuming sulphuric acids, a syrupy solution is formed, which, when diluted with water and saturated with lead carbonate, yields two crystalline lead salts. The acid obtained from the less soluble of these salts forms a *potassium* salt, $C_{10}H_6Cl{\cdot}SO_3K$, which crystallises in thin plates, and by treatment with phosphoric chloride, yields the chloride $C_{10}H_6Cl{\cdot}SO_2Cl$; this crystallises from benzene in tufts of prisms, melts at 108·5—109·5°, and by the action of a further amount of phosphoric chloride, yields ε-dichloronaphthalene.

The acid obtained from the more soluble lead salt forms a *potassium* salt, $C_{10}H_6Cl{\cdot}SO_3K$, which crystallises in rhombic scales; the *barium* salt, $(C_{10}H_6Cl{\cdot}SO_3)_2Ba + 4H_2O$, forms pearly scales. The chloride, $C_{10}H_6Cl{\cdot}SO_2Cl$, forms long needles, melts at 129°, and by crystallisation from excess of phosphoric chloride, yields the dichloronaphthalene, melting at 61·5°. A. P.

Compounds of Guanidine with Diketones. By W. Wense (*Ber.*, **19**, 761—763).—*Phenanthraquinonediguanyl*,

$$\begin{matrix} C_6H_4\cdot C : N\cdot C(NH)NH_2 \\ | \quad\quad | \\ C_6H_4\cdot C : N\cdot C(NH)NH_2 \end{matrix},$$

is prepared by boiling a mixture of a hot alcoholic solution of phenanthraquinone (1 mol.) with an aqueous solution of guanidine carbonate (2 mols.) for a short time. It crystallises from water in yellow prisms, which become colourless when washed with ether. Prolonged boiling with water decomposes it with formation of phenanthraquinone. The *hydrochloride* forms long needles.

Benzilguanyl, $COPh\cdot CPh : N\cdot C(NH)NH_2$, crystallises from alcohol in white, oblong plates; it is insoluble in water.

Benzildiguanyl, $C_{16}H_{16}N_6$, forms crystalline granules, soluble in water. The *hydrochloride* crystallises in long needles. The *platinochloride* is described. N. H. M.

Dimethylanthrachrysone. By E. L. Cahn (*Ber.*, **19**, 755—757; compare Abstr., 1883, 1121; and *Ber.*, **18**, 2142).—Dimethylanthrachrysone is prepared by heating cresorsellinic acid with sulphuric acid (10 parts) at 100°, until the whole has become thick; the product is poured into water, filtered, and washed. It is then dissolved in baryta-water, precipitated by hydrochloric acid, and recrystallised from alcohol. It forms small needles, of bronze lustre. The yield is about 33 to 50 per cent. of the weight of cresorsellinic acid employed. It does not melt at 360°, and sublimes with difficulty in reddish-yellow plates. It is readily soluble in warm amyl alcohol, acetone, chloroform, &c., sparingly in ether and carbon bisulphide, and is insoluble in water and benzene. Caustic alkalis, ammonia, and lime-water dissolve it with yellow coloration. The solution of a trace of the substance in sulphuric acid has a splendid red colour, and, when sufficiently diluted, shows two absorption-bands in the green part of the spectrum, The *tetracetyl-derivative*, $C_{14}H_2Me_2O_2Ac_4$, forms canary-yellow needles, with a vitreous lustre, melting at 234°, and readily soluble in hot glacial acetic acid and alcohol. N. H. M.

Pentahydroxyanthraquinone and Anthrachrysone. By E. Noah (*Ber.*, **19**, 751—755).—These substances are obtained, together with rufigallic acid, by heating equal weights of gallic acid and symmetrical dihydroxybenzoic acid with ten times the weight of concentrated sulphuric acid for 10 to 15 minutes at 160—170°, and pouring the product, while still hot, into a large quantity of water. In separating these hydroxyanthraquinones, use is made of the greater solubility of the acetyl-derivative of the penta-compound in alcohol and of the insolubility of rufigallic acid in dilute alcohol.

Pentahydroxyanthraquinone, $C_{14}H_3O_2(OH)_5$ [1 : 2 : 3 : 1′ : 3′], crystallises in small, red prisms, does not melt at 360°, sublimes, with slight carbonisation, in yellowish-red plates, is readily soluble in acetone and boiling alcohol, sparingly in ether and acetic acid, and is nearly insoluble in benzene, xylene, chloroform, light petroleum, and

boiling water. Concentrated aqueous alkalis dissolve it with green coloration; and it is readily decomposed when fused with potash. The *pentacetyl* compound, $C_{14}H_3Ac_5O_7$, crystallises in bright yellow, silky needles, melts at 229°, and is readily soluble in hot alcohol and acetic acid.

Pure anthrachrysone crystallises in silky needles, and does not melt at 360°. The *tetracetyl*-derivative, $C_{14}H_4Ac_4O_6$, crystallises in yellowish needles, and melts at 253°. A nitro-product could not be obtained. A. J. G.

Synthesis of Homologues of Anthraquinone. By K. Elbs (*J. pr. Chem.* [2], **33**, 318—320).—When the aluminium salts of the homologues of orthobenzoylbenzoic acid, obtained by the action of aluminium chloride on phthalic anhydride and aromatic hydrocarbons, are heated for a minute at 100—110° with concentrated sulphuric acid, and the solution then poured into excess of dilute soda, the anthraquinones are precipitated as dirty yellow powders; or if the heating with the acid has been continued too long, the corresponding sulphonic acids are formed.

In this way, *methylanthraquinone* was prepared from paratoluylorthobenzoic acid, *α-meta-β-dimethyllanthraquinone* from metaxyloylorthobenzoic acid, and impure *α*-methyl-*α*-propylanthraquinone from paracymoylorthobenzoic acid. A. P.

Borneol and Camphor. By Lextreit (*J. Pharm.* [5], **13**, 265—267).—The author has shown (*J. Pharm.* [5], **12**, 211) that thymene picrate when treated with a boiling aqueous solution of soda is decomposed with the formation of a white sublimate, similar in appearance to that obtained under the same circumstances from essence of terebenthene. The substance thus obtained has the formula $C_{10}H_{18}O$. It is lævorotatory, $[\alpha]_D = -37° 21'$, when dissolved in alcohol of 92°, at a temperature of 22°. Its melting point is 200—201°. This lævoborneol gives a lævo-camphor which fuses at 176°, and boils at 204°, closely agreeing with dextro-camphor. J. T.

Camphylamine. By H. Goldschmidt and L. Schulhof (*Ber.*, **19**, 708—714, comp. this vol., p. 249).—*Camphylamine platinochloride*, $(C_{10}H_{19}N)_2,H_2PtCl_6$, crystallises in golden-yellow plates, and decomposes at 200° without melting. The *mercuriochloride*, $C_{10}H_{19}N,HHgCl_3$, crystallises in colourless, lustrous, orthorhombic plates. The *picrate* crystallises in slender, yellow needles, and melts at 194° with total decomposition. The sulphate, oxalate, and dichromate are also described. *Benzoylcamphylamine*, $C_{10}H_{17}\cdot NHBz$, crystallises in colourless prisms, and melts at 75—77°. Ethyl iodide acts on camphylamine, converting it into a mixture of the hydriodides of several bases.

Camphylphenylthiocarbamide, $NHPh\cdot CS\cdot NH\cdot C_{10}H_{17}$, prepared by the action of phenylthiocarbimide on camphylamine, both in ethereal solution, crystallises in short, compact, colourless, lustrous prisms, melts at 118°, and is readily soluble in alcohol and benzene, more sparingly in ether, very sparingly in light petroleum.

Camphylamine dithiocamphylcarbamate, $C_{10}H_{17}\cdot NH\cdot CSS\cdot NH_3\cdot C_{10}H_{17}$,

is obtained by the action of carbon bisulphide on camphylamine as a voluminous white precipitate, which softens at 110° and melts at 116°. When boiled with aqueous soda, it yields the *sodium* salt,

$$C_{10}H_{17}\cdot NH\cdot CSSNa + 3H_2O;$$

this crystallises in silky white plates. *Camphyl thiocarbimide* is obtained in small quantity, when the product of the action of carbon bisulphide on camphylamine is distilled with a solution of mercuric chloride. A. J. G.

Daphnetin. By O. Jung (*Chem. Centr.*, 1886, 41—42).—Daphnetin, melting at 254°, contains 5·38 per cent. water, and hence differs from æsculetin. Daphnetin yields *monethyl-*, *diethyl-*, and *dimethyl-derivatives*, melting at 155°, 72°, and 116° respectively; hence it contains two hydroxyl-groups.

Monobromodiethyldaphnetin, $C_{13}H_{13}O_4Br$, melts at 115°, and by treatment with alcoholic potash is converted into *diethyldaphnetilic* acid, $C_{13}H_{14}O_5$, melting at 154°. This acid combines with hydrogen, yielding hydrodaphnetilic acid.

Diethyldaphnetone, $C_{12}H_{14}O_3$, is formed by distilling the calcium salt of diethyldaphnetilic acid or by heating its silver salt at 308°; it boils at 260°.

Diethyldaphnetin when mixed with alcoholic soda and evaporated, yields a crystalline sodium salt, probably of diethoxycoumaric acid; when treated with methyl iodide, the ethyl salt of *β-triethyldaphnetic acid* is formed; the free acid melts at 193°, and is converted by nascent hydrogen into *triethoxyphenylpropionic acid* (hydrotriethyldaphnetinic acid), melting at 85°. *α-Triethyldaphnetic acid* is obtained by digesting diethyldaphnetin (1 mol.), potash (2 mols.), and ethyl iodide (2 mols.) in alcoholic solution at the ordinary temperature; after suitable purification it melts at 173°; it is exceedingly readily changed to the β-acid.

Triethyldaphnetic acid when oxidised with potassium permanganate yields *triethoxybenzoic acid*, $C_{13}H_{18}O_5$, m. p. 100·5°, and its aldehyde m. p. 70°. This acid is identical with the triethylpyrogallolcarboxylic acid of Will and Albrecht (Abstr., 1884, 1335).

From these reactions, it follows that daphnetin has the constitution $C_6H_2(OH)_2{<}^{CH:CH}_{O—CO}{>}$ [CH : O : OH : OH = 1 : 2 : 3 : 4]. H. B.

Yellow Colouring Matter of Poplar Wood. (*Chem. Centr.*, 1886, 159—160.)—The colouring matter is the same as that of *Erica vulgaris*. It is prepared by boiling for half an hour 10 kilos. of cut twigs, 1 kilo. of alum and 30 litres of water. The turbid liquid clears after a time, and the filtrate exposed to the air and light for 3—4 days acquires a fine golden-yellow colour. The solution can be at once used for dyeing yellow and orange shades, may be mixed with other colours, or may be precipitated and then printed. H. B.

2 : 6-Dimethylpyridine and the Corresponding Dicarboxylic Acid. By C. F. Roth and O. Lange (*Ber.*, **19**, 786—791; comp.

Abstr., 1885, 557).—A direct comparison of lutidine from coal oil with lutidine prepared as described by Epstein (this vol., p. 256), showed that the two are identical. Lutidine boils at 142—143°. The aurochloride melts at 124·5°; the platinochloride forms monoclinic crystals: $a : b : c = 0{\cdot}8921 : 1 : 0{\cdot}6601$; $\beta = 81° 54{\cdot}5'$; melts at 208°, and is isomorphous with picoline platinochloride.

In the preparation of lutidine by Epstein's method (*loc. cit.*), diphenyl is also formed.

Lutidine from either source, when oxidised, yields 2:6 pyridinedicarboxylic acid (Ladenburg and Roth, *loc. cit.*); this crystallises in two forms—long hair-like lustrous needles and hard lustrous prisms—either of which can be readily converted into the other. The prisms are more sparingly soluble than the needles. Both melt at 226°.

The author intends investigating beronic acid, in order to show its identity with one of the dicarboxylic acids of known constitution.

N. H. M.

Orthodimethylpyrrylphenol and Metadimethylpyrrylbenzoic Acid. By C. Paal and C. W. T. Schneider (*Ber.*, **19**, 558—560).—*Orthodimethylpyrrylphenol*, $OH^{2}{\cdot}C_6H_4{\cdot}N^{1}{<}\begin{matrix}CMe : CH\\CMe : CH\end{matrix}{>}$, is obtained by warming the calculated amounts of orthamidophenol and acetonylacetone dissolved in a little absolute alcohol. The whole is poured into water, and the crystalline precipitate dissolved in caustic soda; the solution is then treated with carbonic anhydride which precipitates the pyrroline-derivative in small slender needles. It crystallises from alcohol in white lustrous needles, which after some time become red; it melts at 95°, and is sparingly soluble in water, readily in alcohol, ether, benzene, acetic acid, &c., and in concentrated mineral acids. The *sodium salt*, $C_6H_8N{\cdot}C_6H_4ONa$, and the *picrate* were prepared. Dimethylpyrrylphenol gives the characteristic pyrroline reaction with sulphuric acid and pine-wood (comp. this vol., p. 332).

Metadimethylpyrrylbenzoic acid, $COOH^{3}{\cdot}C_6H_4{\cdot}N^{1}{<}\begin{matrix}CMe : CH\\CMe : CH\end{matrix}{>}$, is formed when acetonylacetone and metamidobenzoic acid are dissolved in a little absolute alcohol and heated for a short time; the liquid is then poured into dilute acetic acid and the precipitate crystallised from alcohol. It forms small crystals, melting at 134—135°, sparingly soluble in water, readily in alcohol, ether, benzene, &c.; it shows the pine-wood reaction very distinctly. When warmed with glacial acetic acid, phenanthraquinone, and sulphuric acid, it acquires a reddish-brown colour. The *alkali salts* are readily soluble in water.

N. H. M.

Products of the Action of Hypochlorous Acid on Quinoline and Substituted Quinolines. By E. Erlenmeyer and J. Rosenhek (*Ber.*, **19**, 489—490).—When quinoline is treated with a solution of bleaching powder, either alone or mixed with a cobalt salt, nearly pure carbostyril is formed. If free hypochlorous acid is employed instead of the bleaching powder, various other products are formed as well as carbostyril, of which at present there have been isolated a di-

and a tri-chloroquinoline, a mono- and a tri-chlorocarbostyril, and volatile acids of the formic and acrylic series.

Crystalline substances have also been prepared from quinanisoïl. Details are reserved for a later communication. A. J. G.

Quinoline-derivatives. By W. v. Miller and F. Kinkelin (*Ber.*, **19**, 525—535).—Homologues of cinnamaldehyde containing a fatty group in the α-position, on condensation with primary amines, will yield a series of quinoline-derivatives containing a phenyl-group in the 2′-position and a fatty radicle in the 3′-position. Such α-derivatives of cinnamaldehyde can be prepared by the action of fatty aldehydes on benzaldehyde in the presence of soda.

α-Methylcinnamaldehyde, CHPh : CMe·COH, is prepared by dissolving 100 grams of benzaldehyde in a litre of alcohol, diluting with 5 litres of water, and adding 58 grams of propaldehyde and 70 grams of 10 per cent. aqueous soda; the reaction is complete in 24 hours. It is a clear yellow liquid of odour similar to that of cinnamaldehyde, boils at 150° under 100 mm. pressure, reduces ammoniacal silver solution, combines with sodium hydrogen sulphite and unites with phenylhydrazine to form a compound $C_{16}H_{16}N_2$, crystallising in flat, yellow needles, and melting at 137°. When oxidised with silver oxide, it yields phenylcrotonic acid.

Phenylmethylquinoline, C_9NH_5MePh [Ph : Me = 2′ : 3′], is obtained by heating 40 grams of methylcinnamaldehyde with 25 grams of aniline and 25 grams of concentrated hydrochloric acid for four hours at 200°; the product is dissolved in alcohol, resinous matters separated by addition of water, the clear yellow solution decomposed by soda, and the base extracted with ether. After further purification, it crystallises in concentrically-grouped, colourless, rhombic prisms, melts at 52—53°, distils above 300°, is insoluble in water, very readily soluble in alcohol, ether, benzene, and light petroleum. The *platinochloride*, $(C_{16}H_{13}N)_2,H_2PtCl_6$, crystallises in reddish-yellow plates; the *picrate* forms large, yellow plates, melting at 202°, the *chromate* crystallises in red prisms. The base is isomeric with the flavoline of Rudolph and Fischer (Abstr., 1882, 1067), and the γ-phenylquinaldine of Geigy and Königs (*ibid.*, 1885, 1236).

A bye-product of the preparation of methylphenylquinoline is left in the aqueous alkaline solution after removal of the base with ether, and can be separated by saturation with salt. It crystallises in slender needles, and yields an amorphous platinochloride of the formula $(C_{19}H_{17}N)_2,H_2PtCl_6$.

Metanitro-α-methylcinnamaldehyde, $NO_2·C_6H_4·CH$: CMe·COH, prepared in a manner similar to that above described, crystallises in thin colourless prisms or needles, melts at 83°, is readily soluble in ether, benzene, and light petroleum, sparingly in hot water, and reduces ammoniacal silver solution. The *phenylhydrazine-compound*, $C_{16}H_{15}N_3O_2$, crystallises in lustrous, golden-yellow needles, melts at 135°, and turns red on exposure to light. The *anilide*,

$$NO_2·C_6H_4·CH : CMe·CH(NHPh)_2,$$

crystallises in yellow needles and melts at 170°.

Metanitrophenylmethylquinoline, $C_9NH_5Me{\cdot}C_6H_4{\cdot}NO_2$ [$C_6H_4{\cdot}NO_2$: Me = 2′ : 3′], is prepared in a manner similar to phenylmethylquinoline; it crystallises in small plates, melts at 145°, and is readily soluble in hot alcohol and in benzene, sparingly in ether or light petroleum. The *hydrochloride* crystallises in concentric groups of prisms; the *platinochloride*, $(C_{15}H_{12}N_2O_2)_2,H_2PtCl_6 + 2H_2O$, forms long needles.

Metamidophenylmethylquinoline, $C_9NH_5Me{\cdot}C_6H_4{\cdot}NH_2$, isomeric with flavaniline, is obtained by reducing the nitro-compound with tin and hydrochloric acid, &c. It crystallises in prisms, melts at 115°, and is readily soluble in alcohol and benzene, moderately in ether. It is a diacid base; the *hydrochloride*, $C_{16}H_{14}N_2,2HCl + 2H_2O$, crystallises in lustrous yellow prisms, the *platinochloride* crystallises with 2 mols. H_2O in rhomboidal orange tables or in anhydrous, yellow plates.

Metamidophenylmethylhydroquinoline is obtained by heating the preceding compound with tin and hydrochloric acid for two to three hours on the water-bath. Neither the free base nor its salts could be obtained in the crystalline form. A diacetyl-compound, $C_{16}H_{16}N_2Ac_2$, was obtained by heating the free base with acetic anhydride; it crystallises in thin, colourless prisms, melts at 178°, and is insoluble in acids.

A. J. G.

Diphenylquinolylmethane. By O. Fischer and A. Fränkel (*Ber.*, **19**, 749—750).—*Diphenylquinolylmethane*, $C_{22}H_{17}N$, is prepared by heating 1 part of amidotriphenylmethane sulphate with 4 parts of glycerol, 4 parts of concentrated sulphuric acid, and 1 part of nitrobenzene. After purification, it crystallises in colourless prisms, melts at 103—104°, and is readily soluble in alcohol, ether, and benzene, sparingly in light petroleum. It shows marked basic properties; the sulphate and hydrochloride are sparingly soluble and crystalline; the platinochloride crystallises in yellowish-red plates. A. J. G.

Quinoxalines (IV). By O. Hinsberg (*Ber.*, **19**, 483—488).—Hydroxydihydrotoluquinoxaline (this vol., p. 82) when freshly prepared melts at about 95°, but so readily suffers alteration that it is impossible to assign a melting point with any certainty. This change seems to be due to oxidation, by which the substance is gradually converted into a *hydroxytoluquinoxaline*, melting at 264°; this seems not to be identical with that melting at 141°, previously described by the author (Abstr., 1885, 909). This substance is also formed from the sodium-derivative of hydroxydihydrotoluquinoxaline by heating for some time at 100—110°, or by passing air through the aqueous solution. It is sparingly soluble in water, readily in alcohol. The dihydrohydroxytoluquinoxaline obtained by Plöchl by reduction of orthonitrotolylglycin (this vol., p. 351) is not identical with the author's compound, and it is doubtful whether it is a definite substance.

Methyltoluquinoxaline, $C_6H_3Me{<}\begin{matrix}N{=}CH\\N:CMe\end{matrix}{>}$, is obtained by slowly adding chloracetone (2 mols.) to an aqueous solution of metaparatoluylenediamine heated at about 60°. It forms white crystals which assume a red colour on exposure to air, melts at 54°, boils at 267—269° (uncorr.), has a quinoxaline-like odour and burning taste, and is

soluble in all proportions in cold water, alcohol, ether, &c.; on warming the aqueous solution, it is in great part precipitated. It closely resembles quinoxaline in its reactions. The *platinochloride*, $(C_{10}H_{10}N_2)_2,H_2PtCl_6$, crystallises in yellow needles. If chloracetone and toluylenediamine are mixed without addition of a solvent, tarry matters are also formed, as well as small quantities of a liquid base boiling at 278—282°, which seems to be a hydroquinoxaline-derivative.

Isatylenetoluquinoxaline, $C_{15}H_{11}N_3$, is prepared by heating isatin with toluylenediamine (equal mol.). It forms a voluminous network of yellow needles, melts at about 290°, is sparingly soluble in alcohol, moderately in ether and chloroform, readily soluble in glacial acetic acid, and insoluble in water and alkalis; it dissolves with brown coloration in concentrated acids, but is reprecipitated on addition of water. A. J. G.

Oxidation Products of Conine. By J. Baum (*Ber.*, **19**, 500—512).—The preparation of benzoylhomoconic acid by the oxidation of the benzoyl-derivative of conine has already been described (Abstr., 1885, 176). The ethyl salt, $C_{17}H_{25}NO_3$, crystallises in long, white prisms, melts at 95°, is readily soluble in alcohol, ether, chloroform, and ethyl acetate, nearly insoluble in water and light petroleum.

Homoconic acid, $C_8H_{17}NO_2$, is prepared by heating benzoylhomoconic acid with hydrochloric acid for four to five hours at 170—180°, and treating the hydrochloride so formed with moist silver oxide. It forms white crystals, melts at 158° with decomposition into its anhydride, is readily soluble in alcohol and water, insoluble in ether; the aqueous solution has a neutral reaction. It is destitute of poisonous properties and is optically inactive. The hydrochloride could not be crystallised; it forms a brown, viscid, very hygroscopic mass, readily soluble in water and ether. The platinochloride, $(C_8H_{17}NO_2)_2,H_2PtCl_6$, is readily soluble in water and alcohol. When heated with soda-lime, a mixture of oily bases is obtained. It does not yield a distinct isonitrile reaction when heated with chloroform and alcoholic potash. When treated with nitrous acid in the cold, an abundant evolution of nitrogen occurs, but the hydroxy-acid which seems to be first formed suffers rapid decomposition into a mixture of other compounds. The author provisionally suggests the formula $NH_2{\cdot}CHPr^{\alpha}{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$ for homoconic acid.

Homoconic anhydride, $C_8H_{15}NO$, is prepared from the acid by heating it to the melting point, or by treating it with absolute alcohol, or even by evaporating its aqueous solution. It forms white crystals, melts at 84—85°, can be sublimed, and is readily soluble in water, alcohol, ether, and chloroform, somewhat more sparingly soluble in light petroleum; it is reconverted into the acid by boiling with baryta-water.

The mother-liquors from the preparation of benzoylhomoconic acid contain benzoic acid and a substance which could not be obtained in a pure state, but when boiled with hydrochloric acid is converted into benzoic acid and Lipp's normal α-amidovaleric acid, $NH_2{\cdot}CHPr^{\alpha}{\cdot}COOH$ (Abstr., 1882, 709). The formation of this substance points not only

to the presence of the normal propyl-group in conine, but also to its occupying the ortho-position relatively to nitrogen, and confirms the proofs already advanced by Hofmann (Abstr., 1884, 1200) and by Ladenburg (*ibid.*, 1885, 176) that conine is a homologue of piperidine. The constitution of conine may therefore be represented by the formula $CH_2<\begin{matrix}CH_2\cdot CHPr^{\alpha}\\CH_2—CH_2\end{matrix}>NH$.

So far, the following substances have been obtained by the oxidation of benzoylconine:—Benzoylhomoconic acid, the benzoyl-derivative of normal α-amidovaleric acid, benzamide, benzoic acid, oxalic acid, butyric acid, a non-volatile syrupy acid, carbonic anhydride, and ammonia. A. J. G.

Morphine. By O. Fischer and E. v. Gerichten (*Ber.*, **19**, 792—795).—20 grams of morphine methiodide were boiled with 200 grams of acetic anhydride until all was dissolved, and the calculated quantity of finely powdered silver acetate (about 7·5 grams) added. The whole was then boiled for 4 to 5 hours, filtered, and the filtrate heated for some hours at 180°. The greater part of the acetic anhydride was then distilled off and the residue poured into water; this, when extracted with warm ether, yielded a *compound*, $C_{18}H_{14}O_4$. The latter forms splendid, white needles, melts at 159°, is insoluble in water, acids, and alkalis, and sublimes unchanged. When oxidised, it yields a product which gives Laubenheimer's phenanthraquinone reaction. When the compound is heated with alcoholic ammonia at 100°, the two acetyl-groups are eliminated with formation of a *compound*, $C_{14}H_{10}O_2$. This separates from water (previously freed from air and kept in an atmosphere of carbonic anhydride) in almost colourless crystals melting at 143°. It is very unstable and is readily oxidised by ferric chloride, Fehling's solution, &c. When a solution of the compound in sulphuric acid is treated with a drop of nitric acid, it acquires a red colour; morphine reacts analogously.

Codeïne, when treated in the way described above, yields a *compound*, $C_{17}H_{14}O_3$. This crystallises from alcohol in long needles which melt at 131°; it is sparingly soluble in water, insoluble in dilute acids and alkalis. The solution in sulphuric acid has an intense yellow colour and when heated acquires a blue fluorescence. The substance is also formed by boiling methocodeïne and ethocodeïne with acetic anhydride, and is identical with the product obtained by Hesse by heating acetylmethocodeïne at 120° (Abstr., 1884, 613). When treated with alcoholic ammonia, it yields a phenol, probably the methyl salt of the compound $C_{14}H_{10}O_2$ described above.

N. H. M.

Hopeïne. By A. Ladenburg (*Ber.*, **19**, 783—785).—Hopeïne is found to be identical with morphine. The specimen obtained by Williamson from wild American hops, and to which the formula $C_{18}H_{20}NO_4,H_2O$ was ascribed (compare *Chem. Zeit.*, 1886, 10, 20, 38, 147), proved to be a mixture of morphine and a more readily soluble base. N. H. M.

Strychnine Chromate. By F. Ditzler (*Arch. Pharm.* [3], **24**, 105—109).—*Distrychnine chromate* is obtained as a reddish-yellow, amorphous precipitate on adding excess of a saturated solution of a normal strychnine salt to a saturated solution of potassium chromate at 15°. Dilute warm solutions give a crystalline precipitate. It can be crystallised in beautiful, orange-yellow needles, which may be heated to 100° without decomposition, but rapidly become discoloured on exposure to light. This salt has the formula $(C_{21}H_{22}N_2O_2)_2,CrO_4H_2$. It is soluble in 469 parts water at 18°, and in 171 parts boiling water, but is insoluble in absolute alcohol, ether, and chloroform.

Monostrychnine chromate is obtained by precipitating a neutral or acidified solution of strychnine by means of a saturated potassium dichromate solution. The amorphous, reddish-yellow precipitate soon becomes crystalline. On recrystallisation from hot water, anhydrous needles are obtained. They are rapidly decomposed under the influence of light, like the previous salt. One part of the salt is soluble in 1815 parts of water at 18°, and in 243 parts boiling water. It is insoluble in absolute alcohol, chloroform, and ether. Analysis indicates the formula $(C_{21}H_{22}N_2O_2)_2,Cr_2O_7H_2$. The author refers to the investigations of Nicholson and Abel (this Journal, 1849, 241). Attempts to obtain other chromates gave negative results. The chromate is not well adapted to the estimation of strychnine; for this purpose the picrate, soluble in 10,000 parts of water at 17°, is better suited. J. T.

Brucine. By A. Hanssen (*Ber.*, **19**, 520—524).—*Nitrobrucine nitrate*, $NO_2{\cdot}C_{23}H_{25}N_2O_4,HNO_3$, is obtained by suspending brucine methiodide in absolute alcohol, heating to boiling, and adding concentrated nitric acid until the methiodide is dissolved; it crystallises in slender, golden-yellow needles, sparingly soluble in alcohol and ether, readily soluble in water; with reducing agents, it gives a violet coloration. When heated in aqueous solution, it gives first a green, then a brown coloration. When treated with sodium sulphite and sulphuric acid, small violet, rhombic plates separate which dissolve in aqueous potash with blue coloration.

Nitrobrucine, $NO_2{\cdot}C_{23}H_{25}N_2O_4$, is formed by the action of sodium carbonate on the nitrate; it crystallises with 4 mols. H_2O in large, ruby-coloured, rhombic forms, or in anhydrous, slender, yellow needles. It does not melt up to 240°, and explodes readily when heated on platinum foil. The platinochloride, $(C_{23}H_{25}N_3O_6)_2,H_2PtCl_6$, crystallises in slender yellow needles.

Amidobrucine hydrochloride, $NH_2{\cdot}C_{23}H_{25}N_2O_4,3HCl$, is obtained by reducing nitrobrucine with tin and hydrochloric acid at the boiling temperature; it crystallises in colourless prisms, and gives with platinum chloride, a yellow, flocculent precipitate which sinters and carbonises at 250—251°. It gives with ferric chloride first a green, then a brown coloration; with dilute potassium dichromate, a transient bluish-violet coloration; and dissolves in concentrated nitric acid to a yellow liquid which turns carmine-red on addition of stannous chloride. The free base was not isolated.

The author is investigating the action of bromine on nitrobrucine. A. J. G.

Aconitine. By A. Jürgens (*Arch. Pharm.* [3], **24**, 127—128, 172).—Aconitine crystallises in anhydrous forms which vary with the nature of the solution from which they have been obtained, whilst from an aqueous solution the aconitine separates in an amorphous form. It has a pricking, burning taste, but is not bitter. It is soluble in about 64 parts of absolute ether, 37 parts of absolute alcohol, 2800 parts of light petroleum of 0·670 sp. gr., $5\frac{1}{2}$ parts of benzene and chloroform, and 750 parts of water. Pure aconitine does not give colour-reactions with phosphoric acid, sulphuric acid and sugar, or phosphomolybdic acid and ammonia, &c., the colours described by some authors being due to resinous substances in the impure material. Aconitine can, however, be readily detected under the microscope as follows:—A minute quantity is dissolved in water, acidified with acetic acid, and a particle of potassium iodide is added; on allowing the solution to evaporate, characteristic crystals of aconitine hydriodide appear, which remain after dissolving out with water the potassium iodide crystals simultaneously formed. The alkaloïd-group reagents act as follows on aconitine solutions. Iodine-water, a reddish-brown precipitate in a solution of 1 : 20000. Potassium mercury iodide, a precipitate in 1 : 10000. Bromimated potassium bromide, potassium bismuth iodide, and iodised potassium iodide, behave similarly. Gold chloride, phosphomolybdic acid and phosphotungstic acid indicate aconitine in a solution of 1 : 5000; picric acid in 1 : 4000; and tannin and potassium nitrite in 1 : 2000. An alcoholic solution of aconitine reduces silver nitrate, but its salts do not thus reduce the silver salt. Analysis of aconitine indicates the formula $C_{32}H_{47}NO_{12}$. J. T.

Bile Acids. By C. Schotten (*Zeit. physiol. Chem.*, **10**, 175—200). Previous researches on the acids of human bile are as follows:—Jacobsen (this Journal, 1874, p. 81) found ordinary cholic acid, glycocine, but no taurine. Hammarsten (*Maly's Jahresb.*, 1878, 263) states that the cholic acid of human bile differs from that of ox bile. Bayer (*Zeit. physiol. Chem.*, **2**, 358; **3**, 292) confirms this, giving the formula of anthropo-cholic acid as $C_{18}H_{28}O_4$; it differs from the cholic acid of ox bile in that its baryta salt is more insoluble.

The author, however, comes to the conclusion that the cholic acid from both sources is identical, and suggests that the apparently smaller solubility of the salts of the acid from human bile may be due to a slight admixture of choleates.

Cholic acid from ox bile crystallises with $2\frac{1}{2}$ mols. H_2O in orthorhombic forms, and not as previously supposed in quadratic crystals. The *methyl* salt, $C_{24}H_{39}O_5Me + MeOH$, crystallises in large, lustrous plates and melts at 110°, or after removal of the alcohol of crystallisation at 147°. The *ethyl* salt, $C_{24}H_{39}O_5Et$, crystallises in needles, melts at 158°, and does not seem to form crystalline compounds with alcohol. Cholic acid is monobasic, does not give acetyl or benzoyl compounds, and on dry distillation gives an anhydride, $C_{48}H_{66}O_3$; this is soluble in alkalis, the solutions when acidified yielding an amorphous acid.

On distilling cholic acid with lime or baryta, an oil which boils below 100° is obtained; this smells like turpentine, suggesting that cholic acid may contain an aromatic radicle. On feeding dogs with bile acids, however, no aromatic acids occur in the urine.

W. D. H.

Cholanic Acid and Bilianic Acid. By P. Latschinoff (*Ber.*, **19**, 474—482).—Cholanic acid is best represented by the formula $C_{25}H_{38}O_7 + \frac{1}{4}H_2O$ (compare Cleve, Abstr., 1881, 750; Latschinoff, *Ber.*, **13**, 1052; and Tappeiner, Abstr., 1879, 388); it crystallises in large, long tables or in flat prisms. 100 parts of absolute alcohol at 18° dissolve 1·37 grams of the acid. The normal barium salt, $(C_{25}H_{35}O_7)_2Ba_3 + \frac{1}{2}H_2O$, in aqueous solution is dextrorotatory, $[\alpha]_D = +49{\cdot}37°$. The acid salts, $C_{25}H_{36}O_7Ba + \frac{1}{4}H_2O$ and

$$(C_{25}H_{37}O_7)_2Ba + \tfrac{1}{2}H_2O,$$

were also prepared.

Triethyl cholanate, $C_{25}H_{35}Et_3O_7$, is obtained by the action of ethyl iodide and ethyl alcohol on silver cholanate: it crystallises in slender, brittle needles, and melts at 75—76°. *Diethyl cholanate*, $C_{25}H_{36}Et_2O_7$, is obtained together with small quantities of tri- and mon-ethyl salts by the action of ethyl iodide and ethyl alcohol on lead cholanate; it melts at 130—131°. The double salts, $(C_{25}H_{35}O_7Et_2)_2Ba + 3H_2O$ and $(C_{25}H_{38}O_7Et_2)_2Pb + 4H_2O$, are described.

Monethyl cholanate, $C_{25}H_{37}O_7Et + \frac{1}{4}H_2O$, is best prepared by boiling the normal salt with dilute aqueous soda; it crystallises in slender needles, melts at 188—190°, and is readily soluble in alcohol, sparingly in ether. The double salts, $C_{25}H_{35}O_7EtBa$ and $C_{25}H_{35}O_7EtPb$, are described.

The *methyl* salts are prepared in a manner similar to and closely resemble the corresponding ethyl salts; trimethyl cholanate melts at 121°; dimethyl cholanate crystallises in tufts of needles and melts at 174—176°; monomethyl cholanate melts at 206—207°.

Bilianic acid forms crystals of the formula $C_{25}H_{36}O_8 + \frac{1}{4}H_2O$ (Cleve described it as containing $4H_2O$; *loc. cit.*). It yields a characteristic hydrogen barium salt, $C_{25}H_{34}O_8Ba$, crystallising in hexagonal tables. Normal methyl bilianate, $C_{25}H_{33}O_8Me_3$, crystallises in lustrous tables or thick prisms, melting at 126—127°. The diethyl salt, $C_{25}H_{34}O_8Et_2 + \frac{1}{4}H_2O$, crystallises in long flat needles and melts at 192—193°. The double salts, $(C_{25}H_{33}O_8Et_2)_2Ba$ and $(C_{25}H_{34}O_8Et_2)_2Pb$, were also prepared.

A. J. G.

Chemistry of the Cell Nucleus. By A. Kossel (*Zeit. physiol. Chem.*, **10**, 248—264).—The question has arisen whether the substance described by Miescher in the yolk of hens' eggs, and named by him *nuclein*, is the same as a similar substance composing in great measure the nuclei of organised cells. They are not the same; by the decomposition of yolk nuclein with weak acids at a high temperature, no bases rich in nitrogen like guanine and hypoxanthine are formed, whereas they are obtained from cell nuclei. In this particular, as also in containing iron, yolk nuclein agrees with milk

nucleïn. These substances cannot be obtained from early embryos, but as incubation goes on, they appear in gradually increasing amount.

Adenine, $C_5H_5N_5 + 3H_2O$ (compare Abstr., 1885, 566, 1080), crystallises in the rhombic system, and is easily soluble in hot water, but only to a slight extent in the cold. The aqueous solution has a neutral reaction. It is insoluble in ether, chloroform, soluble in ferric acetate, and slightly in hot alcohol. It forms compounds with bases, acids, and salts. On heating it with sulphuric acid, hypoxanthine is formed; this is analogous to the change of guanine into xanthine; in each case the reaction consists in the replacement of NH by O.

Adenine is derived from nucleïn, and is an intermediate product between nucleïn and hypoxanthine. It can be obtained from many different animal and vegetable tissues rich in cells; as from tea leaves, spleen, &c. From muscle it cannot be obtained, or only in small quantity; it appears that muscle cells which are poor in nuclei, and have lost to a great extent the morphological characters of cells, have also lost the chemical distinctions of cells; but in those tissues whose cells retain their original character, hypoxanthine and xanthine occur, not uncombined but in union with other groups of atoms, especially with phosphoric acid and proteïds, as part of a still more complex union, nucleïn. The word "differentiation" can thus be applied, not only in a morphological but also in a chemical sense to cells. W. D. H.

Hæmialbumose or Propeptone. By R. Herth (*Chem. Centr.*, 1886, 21—22).—Hæmialbumose is obtained by the action of artificial gastric juice on fibrin; the liquid is neutralised, and the filtrate precipitated by acetic acid and sodium chloride. The author holds that hæmialbumose is a definite substance, and that the differences observed in its action towards reagents depend on the varying amount of acid contained. The addition of 1·8 per cent. (of the dry substance) of hydrochloric acid will dissolve and keep hæmialbumose in solution. From such a solution, the pure substance is prepared by neutralisation and dialysis, followed by precipitation with alcohol. It is believed that hæmialbumose is not formed from fibrin by decomposition with absorption of water, for when pure it has the same composition as fibrin (compare Kühne and Chittenden, Abstr., 1885, 278).

H. B.

Does Water free from Oxygen act on Oxyhæmoglobin? By G. Hüfner (*Zeit. physiol. Chem.*, **10**, 218—226).—This research was undertaken to ascertain whether oxyhæmoglobin gives up any of its oxygen to water from which all air has been thoroughly boiled away. If it did so the spectrum would no longer be that of pure oxyhæmoglobin, but that of a mixture of oxyhæmoglobin and hæmoglobin.

Spectrophotometric observations, however, show that no such dissociation occurs, the hæmoglobin remains in a fully oxygenated condition. When one considers that oxyhæmoglobin easily parts with its oxygen to gases free from that element or in a vacuum, this result at first seems rather unexpected; but as the water used has no air in it,

the oxygen cannot leave the hæmoglobin, or each instant it does so it must immediately reunite with it, both oxygen and hæmoglobin being in solution. W. D. H.

Myohæmatin and the Histohæmatins. By C. A. MacMunn (*Proc. Roy. Soc.*, **39**, 248—252).—The *histohæmatins* are a new class of pigments occurring in the tissues of vertebrate and invertebrate animals. A pigment belonging to this class and found in striped muscle is termed *myohæmatin*.

The tissue to be examined is placed in a compressorium and examined with a Sorby's microspectroscope. The absorption-spectra show at least three bands, one before D, one or two between D and E, and sometimes one or two others nearer the violet. These bands are shown only in the deoxidised condition of the pigments; when they are fully oxidised no bands are seen. The conclusion is drawn that they are concerned in the internal respiration of the tissues and organs where they are found.

Myohæmatin is a reddish-yellow pigment, showing three well-defined bands, λ613—593, λ569—563, and λ556—550. In the oxidised condition, however, no bands are seen. Attempts to isolate the pigment have failed.

Hæmochromogen is found in the medulla of the supra-renal glands of mammals. It is partially removed by washing out the blood-vessels with salt solution. Hence, and owing to the fact it is elsewhere excretory, the hæmochromogen of the adrenals is probably excretory also. If the adrenals are functionless, as in Addison's disease, the metabolism of hæmoglobin and the histohæmatin is prevented, and the incompletely metabolised pigments circulate in the blood and lead to staining of the skin and mucous membranes.

W. D. H.

Poison of Mytilus edulis. By E. Salkowski (*Chem. Centr.*, 1886, 24—26).—The mussels were extracted with hot alcohol; an amount of this solution containing 0·0055 of dry substance was sufficient to kill a rabbit. The poison is not precipitated by platinum chloride, is not volatilised by steam, but is decomposed by boiling with sodium carbonate. The poisonous mussels yield a green alcoholic extract, whilst non-poisonous mussels give a nearly colourless extract; hence the poison is probably contained in the liver. H. B.

Physiological Chemistry.

Feeding Sheep with Raw Sugar. By WERNER (*Bied. Centr.*, 1886, 163—166).—The object kept in view was to estimate if possible the advantage of feeding with raw sugar as against sugar-beet alone or mixed with a small quantity of sugar; of course other fodders were given, linseed cake, &c. The increase in weight occasioned by sugar averaged 0·3 kilo. per 100 kilos., but the cost of the sugar feeding was 53·07 M., whilst that of the root feeding was 40·46, that is, per 1 kilo. live-weight, 1·13 and 1·04 M. respectively.

E. W. P.

Glycogen in the Connective Tissue of Molluscs. By E. R. BLUNDSTONE (*Proc. Roy. Soc.*, **38**, 442—445).—Glycogen occurs in the connective tissue of many molluscs. It can be extracted from the mantle of the Anodon by hot water, and purified by precipitating it several times with alcohol from its aqueous solution. By microscopic examination of the tissues stained with iodine, glycogen is found to be located in the "vesicular cells" (Lankester). The glycogenous vesicles are alone stained, the cell protoplasm and nucleus being colourless. This connective tissue is especially abundant in the neighbourhood of all arteries, hence it is supposed that the specific gravity and nutritive quality of the blood (which is chiefly derived from the water incepted by these animals) is maintained by the discharge of the contents of these vesicles. The molluscan liver is essentially digestive, the glycogenic function of the vertebrate liver being performed by the connective tissue cells. W. D. H.

The Influence of Bodily Labour on the Discharge of Nitrogen. By W. NORTH (*Proc. Roy. Soc.*, **39**, 443—503).—The present experiments, performed by the author on himself, are given with full detail. Each lasted at least 9 days; 4 days of ordinary occupation 1 day work, and a second period of 4 days' ordinary occupation, "Reserve nitrogen" was got rid of by 36 hours' abstention from food or by severe labour before the commencement of the experiment. Observations were made twice daily on the pulse, rate of respiration, temperature of body, and body-weight. The food carefully analysed, weighed, and cooked by the author was taken in four meals, and consisted of bread specially made by the author, dried meat powder, "desiccated potato," "dried julienne," condensed milk, cocoa, "American evaporated apples," "Australian beef marrow," sugar, salt, tartaric acid, and carbonate of soda (for raising the bread). None of these articles of food presented any difficulties as regards analysis. Particulars in the cooking of the food are given. The food, of which there was an unlimited supply, was of *constant composition*, so that for the first time in such experimentation a food, the chemical composition of which was absolutely known, was used. The fæces and urine were collected in specially prepared bottles

carried in a knapsack during walking, which was the special form of work selected. The nitrogen (estimated by combustion with soda-lime), chlorides, sulphates, and phosphates were estimated both in food and excreta. Full particulars of the analyses, pulse, respiration, &c., are given in very exhaustive tables in four experiments made from 1879 to 1883. One of the experiments will serve as an example to illustrate the general results obtained (compare Abstr., 1885, 412).

The following table contains a summary of the full tables given by the author. Experiment 2, June 7—15, 1882; June 11, day of work. Work done, 32 miles walked in 7 hours, the load carried being 27·75 lbs., and the loss of weight after the work 4·5 lbs.

Averages per Diem.

Date.	Urine.			Fæces.	
	P_2O_5.	H_2SO_4.	N.	P_2O_5.	N.
June 7—10.....	1·97	2·75	13·78	2·17	2·26
„ 11.....	1·98	3·65	16·15	—	—
„ 12.....	1·86	3·02	16·31	2·77	2·57
„ 13—15.....	1·78	2·74	14·68	2·25	2·87

Daily Balance of Ingesta and Excreta.

Date.	N of ingesta.	N of excreta.	Difference.	*Total P_2O_5 in excreta. Daily.*
June 7.....	17·64	16·28	1·36	3·54
„ 8.....	35·28	32·76	2·52	4·68
„ 9.....	52·92	48·41	4·51	4·37
„ 10.....	70·57	60·90	9·67	1·80
„ 11.....	88·21	79·62	8·59	4·75
„ 12.....	105·85	98·40	7·45	3·94
„ 13.....	123·50	116·19	7·31	4·25
„ 14.....	141·14	133·68	7·46	3·51
„ 15.....	158·78	150·65	8·13	4·50
Total excreted	—	—	—	35·34
„ ingested	—	—	—	34·84
Difference	—	—	—	0·50

Per diem.	Before work.	After work.	Difference.
Nitrogen in excreta.....	15·22	17·95	2·73
P_2O_5 in excreta	3·59	4·19	0·60
H_2SO_4 in urine	2·74	2·97	0·23

The weights in the above tables are expressed in grams. The results seen are as follows: *nitrogen*, obvious increase on the day of work, continued on the days following it. The reserve at the end of the experiment was only 1·54 grams less than on the day before the work; *phosphoric acid*, the excess of phosphoric anhydride excreted over that ingested (0·5 gram) is probably within the errors of experiment; *sulphuric acid*, the increase after the work is undoubted.

The general conclusions arrived at are as follows:—(1) The results obtained confirm those of Parkes, but the disturbance produced by very severe labour is much more immediate and of greater intensity than that which Parkes observed, probably because the exertion he imposed on the soldiers under observation was inadequate. (3) As in Parkes' experiment, where retention of nitrogen followed the diminution of the nitrogen stored in the body produced by privation of nitrogenous food, so after the disturbance of nutrition produced by severe labour, the immediate effect of which is to diminish the store of nitrogenous material in the system, there follows a corresponding diminution of discharge, the intake being greater than the output. (3) This store of nitrogen is more constantly operative than has been hitherto supposed, thus accumulation took place when the daily supply of nitrogen was not more than 17·6 grams, no extra work being imposed; this amount cannot be regarded as a more than adequate supply for the normal needs of the body. The retention following starvation or exercise is a mere exaggeration of the normal tendency.

A question suggested by the foregoing consideration has still to be worked out, namely, what is the minimum adequate supply of nitrogen? This, which will probably vary with individuals and state of health, might be arrived at by ascertaining to what point the supply of nitrogen could be diminished without drawing on the "reserve nitrogen." This chemical criterion of nutritive vigour would be ascertained by the use of diets, the quantity of nitrogen in which is made less and less until the output becomes equal to the intake. One would then be in a position to say how far the increase of nitrogenous output, the immediate result of labour, is due to previous storage. By means of a work machine invented by the author he hopes to be able to continue his experiments, varying the amount of work per diem and the distribution of the work in time. (4) No increase in the amount of phosphates excreted follows unless the work is very severe. (5) The output of sulphates is proportional to that of nitrogenous material; the amount of sulphates in the food was insignificant. W. D. H.

Estimation of Products of Metabolism in Fæces. By T. Pfeiffer (*Zeit. physiol. Chem.*, **10**, 170—179).—The author protests against the employment of some of his results to support the theories advanced by Stutzer in a recent paper (this vol., p. 377). Artificial digestion with gastric juice is not an accurate method for the estimation of the nutritive value of a food, natural digestion always taking place to a greater extent than artificial. Moreover, the mucin secreted by the alimentary tract being indigestible, will therefore be

reckoned as undigested nitrogenous food. Stutzer states that the difference of the total nitrogen in the fæces, and that insoluble in artificial gastric juice, gives the nitrogen of products of metabolism. The author finds, on the contrary, that the nitrogenous products of metabolism are not completely soluble in gastric juice.

W. D. H.

Formation of Glycuronic Acid during Inanition. By H. Thierfelder (*Zeit. physiol. Chem.*, **10**, 163—169).—The urine of animals which had undergone long privation from food was examined for glycuronic acid. The animals mostly used were rabbits. Kulz has shown that these animals lose all the glycogen in the liver after a six days' fast; the glycogen in the muscles disappears sooner. After this time, glycuronic acid was found in the urine, the tests used being the reduction of copper salts in an alkaline solution, and the action on polarised light. In one dog after a 20 days' fast, the acid was separated from the urine and obtained in a crystalline form. In another dog used in a similar way, grape-sugar but no glycuronic acid was found in the urine. The acid occurred in the urine after the administration of chloral hydrate, camphor, and dimethyl ethyl carbinol, and in rabbits was found to vary in amount from 1 to 3 per cent.

These results are interesting, as showing that carbohydrates are formed from proteïds under these circumstances, and agree in this point with the researches of Seegen (this vol., p. 483) and von Menig (*Archiv Anat. Physiol.*, 1877, 414) who found sugar in the blood during inanition.

W. D. H.

Physiological Action of Boric Acid and Borax. By — Johnson (*J. Pharm.* [5], **13**, 267—269).—The dose of boric acid varied from 0·9 gram to 3·6 grams per day; that of borax was 1·5 grams per day. The action in both cases was not very sensible, excepting sometimes a considerable diuretic increase. With a dose of 3·6 grams, however, intoxication followed. The boron quickly makes its appearance in the urine, and may be detected from eight to 15 days after its employment. The presence of boron in the excrement was very irregular. Three observations showed faint traces in the saliva. Boric acid applied to the skin in an ointment quickly appeared in the urine.

J. T.

Ethyl Carbamate, a New Hypnotic. R. v. Jaksch (*Chem. Centr.*, 1886, 155).—This substance which was first recommended as a hypnotic by Schmiedeberg and Jolly, has been tried by the author in 20 cases. Doses of 0·1 gram induce a certain and quiet sleep, not followed by any evil after effects. It acts essentially on the brain.

H. B.

Chemistry of Vegetable Physiology and Agriculture.

Removal of Micro-organisms from Water. By P. F. Frankland (*Proc. Roy. Soc.*, **38**, 379—393).—In these experiments, samples of water both before and after filtration through, or agitation with various media, were mixed with sterilised nutritive gelatine, the mixture poured out upon a glass plate, and after the lapse of a few days the colonies derived from the individual centres of life counted. Most of the experiments were made with water to which fermented urine was added, others were made with natural potable waters. All precautions necessary for the sterilisation of the apparatus, &c., were taken.

Greensand, coke, animal charcoal and spongy iron were alone found to wholly remove the micro-organisms from water filtering through them, but this power was lost in every case after the filters had been in use for a month, although, with the exception of animal charcoal, these media still effected a considerable reduction in the number of organisms passing through.

A great reduction in the number of organisms is effected by agitating water with various solid materials. Agitation with coke seems to completely remove all organisms.

Clark's process effects a great reduction in the number of suspended organisms. A. J. G.

Studies of Disinfectants by New Methods. By A. W. Blyth (*Proc. Roy. Soc.*, **39**, 259—276).—The conclusions drawn from these experiments are that cresol and phenol have about equal merits as disinfectants, that ferrous sulphate is untrustworthy as a disinfectant, and that with the amines the disinfecting action is in the following order: methylamine, ethylamine, propylamine, and ammonia; methylamine being the most active. Of the pyridine bases, pyridine and parvoline are the most active. The shorter the time a disinfectant acts, the less the disinfection. Disinfection is more active at 35·5—37° than at ordinary temperatures. A. J. G.

Reduction of Calcium Sulphate by Certain Anaërobic Ferments. By Quantin (*Ann. Agronom.*, **12**, 80—86).—The ferment contained in the black liquor of dung-heaps, which has been shown by Dehérain and Gayon to possess the power of attacking cellulose with evolution of marsh-gas, will also reduce calcium sulphate with formation of hydrogen sulphide. Thus 25 grams of chopped straw introduced into a litre flask with 2 grams of calcium sulphate, a few centigrams of ammonium phosphate, and water containing the straw ferment, will soon give rise to considerable quantities of methane and hydrogen sulphide if kept at a suitable temperature (38—40°). Chloroform arrests the production of both gases. The butyric ferment of soils, which Dehérain and Maquenne have shown to possess the power of fermenting sugar into butyric acid and of

reducing nitrates (probably a secondary action of the liberated hydrogen), appears also to have the power of procuring hydrogen sulphide from calcium sulphate to a small extent. Since nascent hydrogen produced by purely chemical processes has no power to effect this reduction, the author believes it is not due to a secondary action, but directly to the ferment. The addition of nitrates prevents the formation of hydrogen sulphide. J. M. H. M.

Note.—The bacterium of some soils and waters which energetically attacks Rochelle salt and in presence of a nitrate totally destroys the nitrate, also has the power of liberating hydrogen sulphide from sulphates. I observed this in two cases in February, 1884; in one case both the ferment and the calcium sulphate were supplied by a well water; in the other case, the ferment was contained in soil, and the sulphur (originally) in potassium thiocyanate, the nitrogen of which had under the influence of the soil suffered complete conversion into nitrate.—J. M. H. M.

A Method of Observing the Respiration of Plants. By U. Kreusler (*Bied. Centr.*, 1886, 115—126).—The apparatus employed is not fully described, but it consisted of an arrangement in which cuttings of plants were exposed to air containing a known weight of carbonic anhydride, then, after the withdrawal of this air, to fresh air free from carbonic anhydride; the plants were either under the influence of ordinary daylight or of an electric light placed at a distance of 45 cm., and of a strength equal to 1000 candles. Previously to acting on the plants, the electric light was freed from heat rays by passage through water. The general results were, that the relative amount (percentage) of carbonic anhydride present is of great importance in the assimilation of that gas, whilst the total or absolute quantity is not of so much importance; commencing with a percentage equal to that contained in the atmosphere the action at first rapidly increases as the percentage rises, but it soon flags, and is finally retrograde. Taking 1 as the percentage of carbonic anhydride in air, and 100 = assimilation, then when the percentage = 7 assimilation = 196, percentage = 17 assimilation 206, percentage 220 assimilation = 230. One of the most important factors in the assimilative power is the presence of moisture in the leaves, and the absence of a sufficiency of moisture is shown directly by the decrease in assimilation long before the leaf flags; this observation largely accounts for the cessation of growth in very dry weather; complete saturation of the air is not detrimental to assimilation, and evaporation from the leaves takes place more rapidly in light than in darkness. It was found that electric light frequently had a greater influence than daylight if the day were very cloudy, and the law of the proportionality between illumination and assimilation was found within a certain range to hold good for the electric light; when the distance of the lamp from the leaves was 1 to 1·5 metres then the amount of gas assimilated hardly balanced the amount expired. As regards expiration in the dark, the researches give no satisfactory answer, but it appears that the presence of carbonic anhydride or

water has but little influence, neither does the amount of water in the plant seem to be of much effect. E. W. P.

Respiration of Plants under Abnormal Conditions. By W. Johannsen (*Bied. Centr.*, 1886, 202—203).—Sudden changes in the pressure of the atmosphere from vacuum to 5 atmospheres do not seem to act prejudicially. If the pressure rises to 2 or 6 atmospheres, then in the first hour a slight increase in the evolution of carbonic anhydride occurs, but later on the evolution diminishes. Plants which have been subjected to prolonged atmospheric pressure and then are placed under ordinary conditions transpire a larger quantity of carbonic acid than they do under the direct influence of the pressure. An increase of evolution of carbonic anhydride occurs after the plant has been at a temperature of 35° and is then brought to the ordinary temperature. If the temperature is 43—45° growth ceases, and there is a reduction in transpiration when the original temperature is attained. E. W. P.

Action of Hydrocyanic Acid on Seeds. By E. Schär (*Chem. Centr.*, **131**, 1885, 826).—The author corroborates Schönbein's experiments on the action of hydrocyanic acid on the germination of seeds; he also finds that this acid arrests the germination, but on its removal germination takes place to an extent almost equal to what it would be if they had only been treated with pure water. He also adds that hydrogen sulphide and mercuric chloride arrest germination, but when the solution is very dilute (0·5 per 1000) 60 to 80 per cent. of the seeds still germinate. E. W. P.

Nectar. By A. v. Planta (*Zeit. physiol. Chem.*, **10**, 227—247).—The nectar of *Protea mellifera* evaporated to a syrup, and thus obtained in large quantities from abroad, contains no nitrogenous matter: 73·17 per cent. of solids, of which 70·08 is grape-sugar, and 1·31 cane-sugar. Grape-sugar was obtained from the syrup in a crystalline form. Besides the sugar, a small amount of formic acid (apparently brought by the bees) and ash was present. The following table gives the percentage of sugar in the fresh nectar of three plants examined.

	Total solids.	Total sugar.	Cane-sugar.	Grape-sugar.
Nectar from *Bignonia radicans.*	15·30	15·27	0·43	14·84
„ *Protea mellifera* ..	17·66	17·06	0·00	17·06
„ *Hoya carnosa*	40·77	40·64	35·65	4·99

Watery extracts of various flowers were also analysed; the small quantity of sugar present in them may be seen from the author's calculation, that in order to obtain 1 gram of sugar (corresponding with 1·3 gram of honey), the bees must suck 2129 flowers of the alpen rose; 2000 of the acacia, *Robinia viscosa*, and 5000 of the *Onobrychis sativa*. W. D. H.

Existence of the Elements of Milk-sugar in Plants. By A. Müntz (*Compt. rend.*, **102**, 624—627).—The crystallisable sugar

arabinose obtained by the action of dilute sulphuric acid on gum arabic has the same rotatory power (+ 80) and the same melting point (167°) as galactose from milk-sugar, and yields a large quantity of mucic acid when oxidised. The so-called arabinose is therefore identical with galactose.

A large number of gums and mucilaginous and pectic substances from different plants which yield mucic acid when oxidised also yield galactose when treated with dilute sulphuric acid. The existence of dextrose in plants is already well established, and it follows that plants contain both the substances which milk-sugar yields on inversion, and from which it is in all probability formed in the bodies of animals. C. H. B.

Phytochemical Studies. By H. Brunner and E. Chuard (*Ber.*, **19**, 595—622).—Glyoxylic acid occurs in grapes in all stages of development; it has also been observed in unripe apples, plums, currants, gooseberries and rhubarb. The leaf stalk of the rhubarb contains a considerable amount of potassium nitrate; succinic acid was also found in it.

The juice of many unripe fruits decolorises iodine solution; this reaction, previously noticed by Buignet in 1861, seems to be due to a compound of glucose and succinic acid; the compound formed by this with iodine, when treated with lead acetate, is resolved into lead iodosuccinate and glucose (? dextrose). The free glucosuccinic acid could not be isolated, being resolved into its components during the process; attempts to synthesise the substance were also unsuccessful. This iodine absorbing substance seems widely disseminated in the vegetable kingdom and occurs most largely in unripe fruit. The greater part of the paper is devoted to a discussion of the nature of the first assimilation product of plants and as to the probability of its being a glucoside. A. J. G.

Composition of the Rind of the Bitter Orange. By Tanret (*Compt. rend.*, **102**, 518—520).—The rinds were extracted with alcohol of 60°, the solution distilled, and the residue agitated with chloroform. The chloroform was then distilled off and the residue treated with cold alcohol which precipitates one constituent, *a*, and dissolves another, *b*. The liquid separated from the first chloroform solution deposits crystals of a third constituent, *c*, and two other substances, *d* and *e*, can be isolated from the mother-liquor.

The substance *a* exists in the rind to the extent of 0·05 per cent., and has the composition $C_{22}H_{28}O_7$. It forms slender, white, tasteless non-volatile crystals, insoluble in water and in ether, only slightly soluble in cold alcohol, but soluble in 100 parts of boiling alcohol and in 60 parts of chloroform. It does not combine with ammonia, but with the other alkalis it forms soluble non-crystallisable salts which are decomposed by carbonic anhydride.

The substance *b* is present to the extent of about 0·1 per cent., does not crystallise, and has an extremely bitter taste. It is almost insoluble in cold water but dissolves readily in boiling water, and is also soluble in ether and in all proportions in alcohol and chloroform. It dissolves in sulphuric acid diluted with its own

volume of water, with formation of a yellow solution, but it does not yield glucose when heated with acids. It has a lævorotatory power $[\alpha]_D = -28$, and its composition is almost identical with that of hesperetic acid.

The substance *c* varies in amount from 0·4 to 3·0 per cent. It crystallises in microscopic needles with a bitter taste, has the same composition as hesperidin, $C_{22}H_{25}O_{12}$, and resembles it in its comparative insolubility in water, but it differs from hesperidin in being much more soluble in boiling water, in alcohol, and in ethyl acetate. The author distinguishes it by the name *isohesperidin*.

The mother-liquor from the isohesperidin contains *aurantiamarin* (C 53·04—53·48; H 6·36—6·16), to which the bitter taste of the rind is due, its amount varying from 0·15 to 0·25 per cent. It dissolves in all proportions in water and alcohol, but is insoluble in ether and chloroform. It resembles hesperidin and isohesperidin in its properties and composition, and has a lævorotatory power $[\alpha]_D = -60°$. The other product from the mother-liquor is hesperidin (0·0 to 0·6 per cent.), which crystallises from boiling alcohol in white silky needles. C. H. B.

Fluorescent Constituent of Atropa Belladonna. By H. Paschkis (*Arch. Pharm.* [3], **24**, 155—158. Compare this vol., p. 156).—The author refers to a paper by Künz (this vol., p. 255). The substance obtained as described in the first Abstract cited above, has the formula $C_{10}H_8O_4$. The author has attempted to obtain metallic compounds of the substance but without success. Experiments made on a dog show that the substance passes into the urine, and probably a portion may be extracted from the liver. J. T.

Feeding Value of Hop Foliage. By Wein (*Bied. Centr.*, 1886, 113—115).—The foliage of hops closely approximates to the composition of meadow and clover hay and rye, and as regards the percentage of proteïn is not far behind wheat and rye bran. Compared with the ordinary green fodders, green hop leaves are a better food. The coefficients of digestion are as follows: albuminoïds, 60 and 70 per cent.; fat, 70—80; and non-nitrogenous matter, 60—75.

E. W. P.

Cultivation of Potatoes. By F. Janowsky (*Bied. Centr.*, 1886, 193—196).—Forty-nine varieties of potatoes were grown, and of these "Round Six Weeks" yielded the highest amount of starch, closely following this were "Magnum Bonum," "Silver Skin," &c. For distillery purposes, the best were "Frühe Nassengrunder," "Early Rose," &c. For cattle fodder "Thusnelda," "Achilles," and "White Elephant," are recommended. E. W. P.

Formation of Methane and Carbonic Anhydride from Cellulose. By F. Hoppe-Seyler (*Zeit. physiol. Chem.*, **10**, 201—217).—The analysis of a large number of gaseous discharges taken from places where the water was pure, but where the soil contained several kinds of vegetable matter, show that marsh-gas composes more than half the volume of the gas collected; the remainder consists of carbonic

anhydride, nitrogen, and in some cases oxygen and hydrogen. The emanation of gas in water-logged soils is increased in warm weather. Observations on Lake Constance showed that the temperature of the air has far more influence than the composition of soil in the production of the gas. The conclusion is arrived at that the chief organic matter which is the source of this gas is cellulose; and that the production of these gases from it is the result of a process of fermentation of a very wide-spread character. The water of the lake contains more solid matter in spring than in the autumn; this, however, is probably due to the dilution of the lake water by glacier water during the summer. If a glass flask, with drawn-out neck, dipping under mercury, be filled with mud containing vegetable remains and water, a mixture of gases may be obtained, consisting of marsh-gas, a large proportion of carbonic anhydride, and, in the first samples of gas evolved, a little nitrogen. This development of gas may go on for months, being increased in amount during hot weather. It is stopped by heating above 60°, or by antiseptics; thus showing the process is due to a ferment.

In nature, the carbonic anhydride diffuses rapidly into the surrounding water, by which it may be dissolved, or where the water is shallow, elaborated by plants, so that the tension of carbonic anhydride on the surface of mud is always kept low. In spring it is diatoms that act thus; they favour diffusion also by their movements; in the summer time other low plants, algæ, &c., replace the diatoms. The author is engaged in further investigations on the influence of this process of gas evolution on the life of organisms and on geological strata. W. D. H.

Manuring Potatoes. By Schrewe (*Bied. Centr.*, 1886, 160—163).—The experiments are of local interest, and were conducted in sandy soil, the manure being Chili saltpetre, put in broad-cast before ridging up, and as a small dose to each plant; also Chili saltpetre with and without superphosphate given in the same way, and farmyard manure. The best result was obtained when the manure was applied to each individual plant; this method also produced the highest percentage of starch. The small potatoes contained least albuminoïds. E. W. P.

Manuring of High-lying Moorlands. By M. Fleischer and others (*Bied. Centr.*, 1886, 100—110).—The moorlands lying in the north-west provinces of Germany, affording only poor feeding for sheep, are cultivated by burning off the top spit, and sowing with buckwheat, after six years' cultivation. They are allowed to rest for 20—30 years. The only manure which appears to be available for the growth of potatoes in this soil after liming, is a mixture of kainite, superphosphate, and Chili saltpetre. The result of such treatment is a net gain of 79 marks per hectare. E. W. P.

Analytical Chemistry.

Estimation of Hydrogen Peroxide. By M. de Thierry (*Compt. rend.*, **102**, 611—613).—The apparatus consists of a small flask with three tubulures, into one of which is fitted a graduated burette with a glass stopcock, whilst the second is connected with the upper extremity of a graduated tube filled with water to the zero mark, and standing in a vessel of water. The third tubulure serves for the introduction of pure powdered manganese peroxide. A definite volume of hydrogen peroxide is run from the burette into the flask containing the manganese peroxide. Decomposition is complete in a few minutes, and the evolved oxygen is collected in the graduated tube, a correction being made for the volume of air displaced by the hydrogen peroxide. C. H. B.

Standardising Iodine Solutions. By W. Kalmann (*Ber.*, **19**, 728—729).—A measured volume of the iodine solution is diluted with water, treated with hydrogen sulphide until decolorised, and the hydriodic acid formed titrated with decinormal soda; the indicator used being methyl-orange, which is not affected by hydrogen sulphide. This method is accurate, and far quicker than the usual method of the comparative titration with sodium thiosulphate of the iodine solution, against a known weight of resublimed iodine. A. J. G.

Estimation of Dissolved Oxygen in Water. By A. Dupré (*Analyst*, **10**, 156—160).—For this purpose, the author uses the process of Schützenberger and Rister slightly modified. The hyposulphite solution is standardised with fully aërated water instead of ammoniacal copper sulphate, the titration is conducted in an atmosphere of hydrogen, and several other precautions are taken against the introduction of adventitious oxygen. When calculating the results, certain numerical corrections have to be made, inasmuch as the rate of oxidation of reduced indigo differs from that of the hyposulphite. D. A. L.

Use of Ammonium Citrate in the Analysis of Precipitated Phosphate. By H. H. B. Shepherd (*Analyst*, **10**, 161—163).—Neutral ammonium citrate is recommended as a solvent in the determination of phosphoric acid in precipitated phosphate, inasmuch as ammoniacal ammonium citrate, although answering well for "reverted" phosphate, only dissolves a portion of the precipitated phosphate, whilst the neutral salt is almost as good a solvent as dilute citric acid for precipitated phosphate, and at the same time dissolves less of the less valuable ground mineral phosphates. D. A. L.

Determination of Arsenic. By L. W. McCay (*Amer. Chem. J.*, **7**, 373—392).—The author confirms the accuracy of Holthof's method (Abstr., 1884, 1428), but recommends that the reduction should be

effected by heating with an equal volume of a saturated solution of sulphurous anhydride in a closed vessel on the water-bath. The reduction is then complete in one hour, whilst four hours' boiling is required in open vessels.

F. Mohr's method of removing arsenic trisulphide from the filter-paper by solution in ammonia, followed by evaporation and weighing the residue, is not accurate, as the sulphide suffers decomposition unless it has been previously dried on the filter-paper.

H. B.

Determination of Carbon and Hydrogen by Means of Copper Oxide Asbestos. By E. Lippmann and F. Fleissner (*Monatsh. Chem.*, **7**, 9—19).—This is a modification of Kopfer's method for combustion by means of platinum asbestos. In place of the latter, very finely divided copper oxide, obtained either by precipitation or by ignition of metallic copper prepared by reduction, well mixed with asbestos, is used. The substance for analysis is introduced in a boat, and the combustion carried on in a stream of air. The method answers with substances containing nitrogen, and a number of analyses are given, showing that accurate results are obtainable with it.

G. H. M.

Separation and Estimation of Copper, Cadmium, Zinc, Nickel, &c. By A. Carnot (*Compt. rend.*, **102**, 621—624).—The solution containing copper, cadmium, and other metals is diluted to 200—300 c.c., acidified with 10—15 c.c. of hydrochloric acid, heated to boiling and mixed with successive portions of ammonium thiosulphate solution until the precipitate remains white and milky, owing to the presence of free sulphur. The precipitate consists of cuprous sulphide, which is treated in the usual way. The cadmium in the filtrate is precipitated by means of hydrogen sulphide or ammonium sulphide.

Cadmium and zinc can be separated in a similar manner, care being taken to prevent precipitation of oxalates along with the sulphide. Zinc oxalate is only slightly soluble in presence of ammonium oxalate, whilst cadmium oxalate forms a double salt which is readily soluble.

The somewhat concentrated solution is neutralised with ammonia, mixed with 10 parts of ammonium chloride for 1 part of metal present (to prevent precipitation of any cadmium oxalate), and an excess of oxalic acid, and heated to boiling. Any zinc oxalate which separates is filtered or decanted off, and washed with a warm solution of ammonium chloride. The liquid is diluted to 200—250 c.c., heated to boiling, and mixed with successive quantities of ammonium thiosulphate until no further precipitation of cadmium sulphide takes place. More oxalic acid is added from time to time if necessary.

The zinc in the filtrate is precipitated by means of hydrogen sulphide, the precipitate mixed with the oxalate previously obtained, and the whole converted into sulphide by heating with sulphur in a current of hydrogen.

C. H. B.

Estimation of Chromium. By H. Vignal (*Bull. Soc. Chim.*, **45**, 171—177).—The sample in which the chromium is to be estimated is,

if a chromium steel, dissolved in nitric acid at 22°; castings of ferro-chromium must, however, be dissolved in dilute sulphuric acid (two of water to one of acid) and nitric acid subsequently added. Chromium minerals or blast furnace slags may be most readily obtained in solution by fusing with sodium carbonate and potassium nitrate for an hour at a red heat, extracting the mass with water, and evaporating the solution to dryness with 10 parts of crystallised ammonium nitrate in order to destroy nitrites and render the silica and alumina insoluble; the dry mass is then extracted with water, acidified with nitric acid, and a concentrated solution of potassium permanganate added to the nitric acid solution thus obtained until the soluble brown precipitate which is at first momentarily produced is replaced by a slight but permanent precipitate of black manganic dioxide; the solution is then filtered through asbestos, treated with excess of a standard solution of ferrous sulphate, and the excess titrated with potassium permanganate. The presence of nitric acid is advisable, as the manganic dioxide is then precipitated in a form in which it may be much more readily filtered and washed. The method is only applicable to samples containing less than 3 per cent. of chromium; with higher percentages, it gives results which are too high, although by introducing suitable corrections they may be obtained within 0·5 per cent. A. P.

Permanganate Test in Water Analysis. By A. Dupré (*Analyst*, **10**, 118—121).—It is now recommended to conduct the treatment with permanganate and phosphoric acid (instead of sulphuric acid) in a closed vessel at 0°, instead of at 80° as previously suggested by the author. By adopting the low temperature, uniformity of method and comparable results are secured, moreover in waters rich in chlorides the tendency to loss is very greatly diminished. The use of phosphoric instead of sulphuric acid is favourable for the subsequent titration with iodine. D. A. L.

Testing for Mineral and Resin Oils in Fat Oils, Oleïns, and Fuller's Fats. By Focke (*Chem. Centr.*, 1886, 44—45).—20 grams of the material is evaporated with 8 to 10 grams of potash and 50 c.c. of alcohol, the soap dissolved and decomposed by acid, and the separated acids, &c., well washed. That portion soluble in ether is then determined. 10 grams of the fatty acids (or mixture) so obtained is dissolved in 50 c.c. of alcohol and aqueous soda (1 : 3) gradually added to neutralisation—using phenolphthaleïn as indicator; to the still liquid mixture 100 c.c. of light petroleum, boiling below 80°, is added and the whole shaken. After some time 500 c.c. of water is added with gentle shaking, the separated soap solution is drawn off, and the petroleum solution washed with 300 c.c. of water; a little alcohol added to the petroleum solution helps it to settle clear. The petroleum solution lastly is gently evaporated to dryness. H. B.

Determination of Glycerol Produced by the Saponification of Fatty Oils. By A. H. Allen (*Analyst*, **11**, 52—54).—10 grams of the fatty oil is treated with 4 grams of caustic potash in 25 c.c. water,

in a bottle securely closed with an indiarubber stopper and heated at about 100° until saponification is complete. Aqueous instead of alcoholic potash is used to avoid the introduction of extraneous oxalic acid. The soap is decomposed in the usual way, and the glycerol determined in half the liquid by Benedikt's method (comp. this vol., p. 395). D. A. L.

Determinations of Mixtures of Milk- and Cane-sugar. By A. W. Stokes and R. Bodmer (*Analyst*, **10**, 62—65).—The reducing sugar is determined by means of Pavy's ammoniacal Fehling solution, in the liquid containing the mixture of milk and cane-sugar both before and after boiling for about 10 minutes with a 2 per cent. solution of citric acid. As this latter treatment inverts the cane-sugar only, the amount of each sugar present can be readily calculated from the numerical data obtained. D. A. L.

Determination of Milk-sugar in Milk. By C. W. Stephens (*Analyst*, **10**, 30—32).—Six to eight grams of milk is made up to 100 c.c. with water, and without any further treatment the milk-sugar is determined in this solution by means of Fehling solution; either volumetrically by running the milk solution from a burette into 25 c.c. of boiling Fehling solution, or gravimetrically by adding a known quantity of milk solution to slight excess of Fehling solution, and determining the amount of copper in the precipitate. The method is convenient and gives good results. D. A. L.

Estimation of Raffinose in Mixtures. By R. Creydt and B. Tollens (*Annalen*, **232**, 205).—The authors expect to be able to determine the percentage of raffinose in molasses by weighing the mucic acid produced by oxidation with nitric acid. W. C. W.

Estimation of Acetic Acid by Distillation in Liquids containing Organic Matter. By H. W. Wiley (*Amer. Chem. J.*, **7**, 417—424).—Duclaux's method, which rests on the assumption that the acetic acid in a solution subjected to distillation gives a definite percentage of its weight in given successive portions of the distillate, is shown to be incorrect, the results being too low. Lactic acid is only carried over by steam to a very slight extent; a distillate of 100 c.c. from a solution measuring 135 c.c. contained but 0·016 per cent. of the acid present, whilst acetic acid passes over to the extent of 7·3—30·1 per cent., according to the total amount of acid present. The author's method of proceeding is as follows:—(1) The sample of sour milk is mixed with an equal volume of alcohol and the total acids in the filtrate determined, using phenolphthaleïn as indicator, the result to be taken at 95 per cent. of the amount present. (2) 100 c.c. of the milk is diluted to 130 c.c. and 100 c.c. distilled off. If 12 c.c. of centinormal caustic soda are required for neutralisation, it can be assumed that 10 per cent. of the acetic acid has distilled over; with 40 c.c. soda solution, 18 per cent. of the acetic acid; with 70 c.c. soda solution, 23 per cent. of the acetic acid; with 110 c.c., 27 per cent., and with 200 c.c., 31 per cent. of the total acetic acid. H. B.

New Method for the Analysis of Milk. By M. A. Adams (*Analyst*, **10**, 46—54).—Five c.c. of milk are run into a tared beaker, conveniently of 30 c.c. capacity and 2 inches high by $1\frac{1}{4}$ in diameter. The charged beaker is weighed, and a tared coil of dry blotting-paper is gently thrust in; as soon as all the milk is sucked up, the paper is withdrawn, and placed dry end downwards upon a glass plate; the beaker is then weighed again. The paper resting in the same position on the glass plate is roughly dried for one hour in a water-oven, is then transferred to a Soxhlet's extraction apparatus with a flask of 150 to 180 c.c. capacity, and is exhausted with ether (or light petroleum). The fat is dried and weighed in the flask, whilst the solids-not-fat are obtained by thoroughly drying the exhausted coil in an air-bath at 100° and weighing. This method, owing to the large surface exposed to the solvent, ensures the complete and rapid extraction of the fat, and moreover, owing to the absence of fat in the residue, the solids-not-fat can be dried to constancy, and hence more thoroughly than heretofore, without the results being vitiated by oxidation. For the latter reason, it is better to determine total solids by the addition of the numbers obtained for fat and solids-not-fat, than by drying the mixture of solids on the paper and weighing. Comparative experiments with other methods bear out the above statements; therefore by this method the fat is always higher, the solids-not-fat always lower; the reduction in the latter, owing to more perfect drying, is in greater proportion than the increase of the former; hence the total solids are also somewhat lower. The coils are prepared from white blotting paper known as "white demy blotting," by cutting it into strips $2\frac{1}{2}$ inches wide and 22 inches long; these are rolled into helical coils of diameter somewhat under an inch. D. A. L.

Use of Acetic Acid in Milk Analysis. By W. Johnstone (*Analyst*, **11**, 22—32).—Five grams of milk is treated with acetic acid and evaporated and dried in a flat-bottomed platinum basin $2\frac{1}{2}$ inches in diameter; the dry matter in the dish being then exhausted in a special apparatus designed by the author. Numerous experiments indicate that the method is quite trustworthy. The statement that milk-sugar becomes anhydrous, but is not decomposed by prolonged exposure to a temperature of 100°, or for half an hour at 108°, is confirmed. Milk-fat, when kept at 100°, at first increases, then subsequently decreases in weight, and the amount of the insoluble fatty acids seems to be considerably diminished by long heating. D. A. L.

Reichert's Method of Examining Butter-fat. By A. H. Allen (*Analyst*, **10**, 103—105).—The author is strongly in favour of this method as a means of "sorting" butters. He points out that it is important that the volume of the acidified liquid before distillation should always bear the same proportion to the volume of the distillate. D. A. L.

Effect of Allantoin on the Estimation of Urea in Urine. By P. Malebra (*Gazzetta*, **15**, 531—534).—In estimating urea in

urine by the sodium hypobromite method, no consideration has hitherto been paid to the presence of allantoin, although it has been shown to occur in certain physiological conditions, especially in the gestation period. Allantoin, when treated with sodium hypobromite at ordinary temperatures, evolves only half its nitrogen as such, resembling its congener, uric acid. Thus in urine determinations the amount of allantoin must be determined by independent methods, and its quantity taken into account in the result of the hypobromite determination. V. H. V.

Colour Reactions of Certain Alkaloïds. By W. Lenz (*Zeit. anal. Chem.*, **25**, 29—32).—Out of 72 alkaloïds examined, the following alone gave characteristic colours when fused with potash (see *ibid.*, **21**, 226):—Quinine gave a grass-green, and at the same time a peculiar odour; quinidine, green, becoming yellower and finally brown; cinchonine, at first brownish-red to violet, with green edges, later bluish-green; cinchonidine, blue, passing into grey; cocaïne, greenish-yellow, turning to blue, and then dirty red on stronger heating. Half a milligram was used in each case. M. J. S.

Adulterations of Saffron. By J. M. Maisch (*Analyst*, **10**, 200—203).—Styles, stamens, and corolla tubes of the saffron flower, meat fibres, petals of pomegranate and of Saponaria and florets of composite flowers are amongst the most common organic adulterants of saffron, whilst chalk, gypsum, and barium sulphate are found as mineral adulterants. These adulterants have frequently to be dyed, for which purpose red saunders or Brazil wood is used. Descriptions of the various organic adulterants are given in the paper. Microscopic examinations, soaking in water and subsequent ocular inspection, coupled with chemical tests with acids, alkalis, testing for tannin, &c., are recommended for the analytical examination of saffron. D. A. L.

General and Physical Chemistry.

Relation between the Absorption-spectrum and Sensitising Action of Dyes on Silver Bromide. By H. W. Vogel (*Ann. Phys. Chem.* [2], **26**, 527—530).—The author has observed that certain dyes when mixed with silver bromide increase its sensitiveness for those rays which they absorb; and the validity of this relation has been confirmed by Becquerel for chlorophyll, and by Waterhouse and Eder for other colouring matters. On the other hand, Meyerschmidt, resting on the single exception of diamidobenzene, has combatted this general conclusion. It is here pointed out that this apparent exception is to be explained by the difference in character of the absorption-spectrum of substances according as they themselves or their solutions are examined; the admixture of foreign material with the dye in the gelatin plate, accompanied possibly by certain chemical changes, would doubtless modify its absorption-spectrum, and concomitantly its sensitiveness for certain light rays. V. H. V.

Fluorescence of Naphthalene-red. By K. Wesendonck (*Ann. Phys. Chem.* [2], **26**, 521—527).—In this paper, the question is discussed whether certain dyes and especially naphthalene- (Magdala) red form exceptions to Stokes's law of fluorescence, in that certain yellow and orange-red rays give rise to fluorescent rays of less refrangibility. It is here shown that the phenomenon is complicated by the formation of an aureole of light, which is probably not caused by the presence of impurities, although it does not appear likely that the complication is sufficient to account for the anomaly.

V. H. V.

Electrical Conductivity of Bases. By W. Ostwald (*J. pr. Chem.* [2], **33**, 352—370).—The author has already shown that all monobasic acids are subject to a general law in relation to the alteration of their molecular conductivity with their dilution. The experiments described in the present paper show that the same law applies also to bases. In the measurements given, the mercury unit employed by Kohlrausch is used.

Potash behaves similarly to the strong acids; the conductivity increases only slightly with dilution, and a maximum is reached between 256° and 512°. The hydroxides of sodium, lithium, and thallium behave similarly, whilst those of the alkaline earths have about twice the conductivity of the alkalis.

Ammonia behaves exactly like the monobasic acids. In methylamine, the basicity is increased to five times that of ammonia; ethylamine has slightly stronger basic properties than methylamine, whilst propyl-, amyl-, and isobutyl-amine are all feebler bases than ethylamine. This relation is analogous to that of the fatty acids (comp. *J. pr. Chem.* [2], **32**, 317). Allylamine has about the same conductivity as ammonia twice as much diluted, hence it would appear

that the radicle C_3H_5 is almost neutral, whilst the radicles C_nH_{2n+1} have undoubtedly basic characters.

Dimethylamine is slightly stronger than methylamine; diethylamine is stronger than dimethylamine, the difference being more marked than in the case of the monamines.

Trimethylamine shows a very considerable reduction in basic power; triethylamine is also a feebler base, but only slightly so.

Measurements of the electrical conductivity of ammonium hydroxides, such as tetrethyl- and phenyltriethyl-ammonium hydroxide, show that these compounds are completely analogous to potash and soda. The substitution of phenyl for ethyl has practically no influence. Triethylsulphine hydroxide, $SEt_3 \cdot OH$, also behaves like soda.

The substances examined may be divided into (1) weak ammonium bases, and (2) strong hydroxides.

Guanidine was found to be more nearly allied to the hydroxides than to the ammonium bases, which can only be accounted for on the supposition that it contains pentadic nitrogen.

Ethylenediamine behaves similarly to such bibasic acids as phosphorous and sulphurous acids, of which the normal salts react alkaline; it cannot be titrated. It is a weaker base than ethylamine. On the other hand, metaphenylenediamine is stronger than aniline, as also is phenylhydrazine.

The reactions of bases as such are ruled by definite coefficients which depend on the nature of the base and not on that of the reaction. Thus it can be predicted that the ammonium bases will follow the alkalis in the saponification of ethyl acetate and in other reactions.

The following conclusions are drawn:—(1) The same general law of dilution holds good for bases as well as for acids. (2) The bases react according to an individual coefficient of affinity, which is nearly proportional to the conductivity. (3) The limit which the conductivity reaches in the case of unlimited dilution is not the same for different bases, but can produce a difference of over 10 per cent. of the amount. N. H. M.

Influence of Pressure on the Resistance of Electrolytes. By J. Fink (*Ann. Phys. Chem.* [2], **26**, 481—517).—The researches of Colladon and Sturm, and of Hering have shown that the resistance of electrolytes is practically unaltered by increase of pressure, whilst the more recent experiments of Lenz indicate a decrease of 0·02 per cent. in resistance for every increase of one atmosphere pressure, a result which would be a probable deduction from the experiments of Röntgen and Warburg on the influence of pressure on the specific viscosity of liquids. The results are here given of experiments with solutions of hydrochloric acid, sodium chloride, and zinc sulphate, of various degrees of concentration, compressed at various pressures up to 500 atmospheres by means of a Cailletet's pump. The apparatus is described in detail. The principal results are as follows:—(i) The resistances of the above electrolytes decrease proportionally with the increase of pressure up to 300 atmospheres; at higher pressures the relative increase is somewhat diminished, although it is allowed that this result may be due to errors in the manometer; the numerical

results are practically in accordance with those of Lenz, although they are somewhat modified by changes in other conditions, such as temperature, concentration of solution, and nature of the substance dissolved. (ii) It is shown by application of the formula $p = \frac{\Delta v}{\mu}$, in which p is the pressure and μ the coefficient of compressibility of a solution, that the change of resistance of a liquid by warming under atmospheric pressure is not conditioned by change of density, but by increase of molecular mobility. V. H. V.

Influence of Temperature on the Electromotive Force of Thermo-electric Couples. By H. Le Chatelier (*Compt. rend.*, **102**, 819—822).—Avenarius and Tait have shown that the electromotive force of a metallic couple increases between 0° and 400°, in accordance with a parabolic function of the absolute temperatures of the two junctions,

$$E = A(T_1 - T_0) + B(T_1^2 - T_0^2),$$

or if one of the two junctions is kept in melting ice,

$$E = at + bt^2,$$

where t is the ordinary temperature of the warm junction, and a and b are constants depending on the nature of the couple.

The author finds that this law holds good for temperatures above 400° up to a certain limit which depends on the nature of the couple, and beyond which the value of the coefficients suddenly changes, whilst the nature of the equation remains the same. Values of the coefficients for platinum and platinum-iridium at different temperatures are given in the original paper. The calculated results agree well with those actually obtained, and any divergencies may be attributed to the well-known irregularities of thermo-electric couples. C. H. B.

Relation between the Specific Heat of Solid Organic Compounds and their Chemical Composition. By H. Kopp (*Ber.*, **19**, 813—811).—At the time that the author published his principal paper on the specific heat of compounds (*Annalen*, *Suppl.-Bd.*, **3**, 329, *et seq.*), it was believed that the specific heat of every substance would be approximately constant if determined at a sufficiently low temperature. He found that for most elements in the solid state (especially the metals and halogens) the "atomic heat" is the same, namely, 6·4, but that for some few elements this is not the case (*i.e.*, C = 1·8, H = 2·3, O = 4, &c.). From his experiments, he concluded that "the molecular heat of a compound in the solid state is the sum of the atomic heats of its compounds, as deduced from their constant specific heats." Later researches have, however, shown that in the case of the apparently abnormal elements, a high and not a low temperature is required in order to get the constant and true specific heat, and that at such temperatures the atomic heat approximates very closely to 6·4. Therefore the above rule requires slight modification, in so far that "in the case of elements whose atomic heats are

approximately constant at low temperatures these constant atomic heats are to be employed, whilst in the case of those elements whose atomic heats become constant only at very high temperatures, their (non-constant) atomic heats at ordinary temperatures are to be employed. Thus for a solid organic compound, $C_cH_hO_oX_x$ (where X represents an element whose atomic heat at low temperatures is 6·4), the molecular heat will be $1{\cdot}8c + 2{\cdot}3h + 4o + 6{\cdot}4x$, and, of course, the specific heat this number divided by the molecular weight.

De Heen has lately (*Bull. Acad. Roy. de Belg.* [3], **5**, 757) published the results of the determination of the specific heats of several solid organic compounds, and in the present communication the author discusses these results, and compares them with the numbers calculated according to his formula. The following table gives this comparison :—

Substance.	Calc. sp. heat.	Sp. heat observed by De Heen.
Succinic acid	0·314	0·308 between 10° and 60°
Methyl oxalate	0·314	0·314 „ 10 „ 35
Sodium formate....	0·272	0·292 „ 10 „ 93
Calcium formate...	0·235	0·242 „ 10 „ 33
Barium formate....	0·135	0·140 „ 10 „ 40
*Potassium acetate..	0·254	0·290 „ 10 „ 30
*Calcium butyrate ..	0·322	0·382 „ 10 „ 70
*Barium valerate....	0·241	0·299 „ 54 „ 92
Zinc valerate	0·306	0·307 „ 10 „ 41
Cryst. zinc acetate, $Zn(C_2H_3O_2)_2 + 3H_2O$	0·292	0·270 „ 15 „ 75
*Crystallised oxalic acid ($C_2H_2O_4 + 2H_2O$).....	0·329	0·422 „ 40 „ 90

The author has obtained numbers almost identical with De Heen's for succinic acid (0·313 between 17° and 51°) and barium formate (0·143 between 18° and 52°).

It will be seen that in the case of seven of the above compounds the calculated numbers agree very closely with those observed, but in the remaining four cases, marked *, great discrepancies are apparent. In the case of potassium acetate, calcium butyrate, and barium valerate, the discrepancies are probably in great part due to the temperatures employed not being low enough to obtain the true and approximately constant specific heat of the *rigid* solid. Thus the specific heat of the acetate increased even between 10° and 40°, and between that point (where softening commenced) and 48°, the increase was very considerable. Neither the butyrate nor valerate could be considered as really constant, even between the temperatures given, and above 70° and 92° respectively the specific heat rose rapidly. But besides this, the author is of opinion that some source of error must have been present in all three cases which caused the figures obtained to be uniformly above the true numbers.

With regard to the fourth case, where the discrepancy is very great,

it would appear that, unless some serious source of error has been overlooked by De Heen, the usual rule is entirely inapplicable to crystallised oxalic acid. L. T. T.

Potassium and Sodium Selenides. By C. Fabre (*Compt. rend.*, **102**, 703—706).—Heat of formation of sodium selenide, dissolved, from dissolved sodium hydroxide and dissolved hydrogen selenide, + 7·60 cal.; from dissolved sodium hydroxide and gaseous hydrogen selenide, + 16·72 cal.

Heat of solution of sodium selenides:—$Na_2Se,16H_2O$, at 14°, − 22·0 cal.; $Na_2Se,9H_2O$, at about 12°, − 10·58 cal.; $2Na_2Se,9H_2O$, − 15·72 cal.; Na_2Se, anhydrous, + 18·62 cal.

Heat of formation of potassium selenide, dissolved, from dissolved potassium hydroxide and dissolved hydrogen selenide, + 7·52 cal.; from dissolved potassium hydroxide and gaseous hydrogen selenide, + 16·92 cal.

Heat of solution of potassium selenides:—$K_2Se,19H_2O$, at about 14°, − 29·30 cal.; $K_2Se,14H_2O$, at about 13°, − 20·44 cal; $K_2Se,9H_2O$, at about 14°, − 19·20 cal.; K_2Se, anhydrous, + 8·54 cal.

If these results are combined with Hautefeuille's value for the heat of formation of hydrogen selenide, + 5·4 cal., the following values can be deduced: heat of solution of hydrogen selenide, + 9·26 cal.; heat of formation of sodium selenide, solid, from the solid elements, + 78·90 cal.; heat of formation of solid potassium selenide from the solid elements, + 98·34 cal.

The difference between the heats of formation of the two selenides is similar to the difference between the heats of formation of the corresponding sulphides, chlorides, bromides, iodides, and cyanides. C H. B.

Thermochemical Analysis of the Reaction between Alum and Potassium Hydroxide. By A. V. E. Young (*Amer. Chem. J.*, 8, 23—46). — Thomsen gives the heat evolved in the reaction $Al_2(SO_4)_3,K_2SO_4 + 6KOH = 4K_2SO_4 + Al_2(OH)_6$ as 30·528 cal.; even though the whole of the alumina is precipitated by only 5 mols. of potash; in this paper, it is shown that the decomposition is not so simple as is indicated by the above equation. The general method of heat measurement is that described by Berthelot. A series of experiments made by adding increasing amounts of potash (from 0·5 to 10 mols.), and another made by adding increasing amounts of sulphuric acid to a mixture of alum with an excess of potash, showed that the main result is complicated by the solution in the residual alum of the precipitate first thrown down, by the precipitation of basic salts, and by the solution of the precipitate by the potash. The composition of the precipitates produced was found by analysing the filtrates, since washing the precipitates was not admissible; the precipitation begins with 1·3 mol. of potash, is complete with 4·8 mols., and the precipitate is redissolved by 8·1 mols.; the precipitate contains sulphuric acid until 7 mols. of potash have been added. The results obtained are independent of the method of procedure, and depend only on the amounts of materials taken which react among each other until equilibrium is attained. It is also shown

that rise in temperature or increase of dilution tends to remove acid from the precipitate, without, however, increasing the amount of alumina precipitated; time does not affect the equilibrium whilst the original precipitate remains in the system. H. B.

Boiling Point and Pressure. By G. W. A. Kahlbaum (*Ber.*, **19**, 943—949).—This paper is an answer to the criticisms of Ramsay and Young (this vol., pp. 5 and 410) on the author's contention that the statical and dynamical methods do not give identical results. In it, experiments are described on the boiling point of normal butyric acid under reduced pressure by means of an apparatus which consists in outline of two manometers in connection with one another, one of which is blown out at its upper extremity, so as to contain the liquid to be examined, the vapour-tension of which is simultaneously exerted on the other manometer. There was practically no important difference in the readings of the two manometers when the liquid was made to boil. But at a pressure of 13 mm. the temperature of ebullition was found to be 67°; whilst Landoldt found under the same conditions a temperature of 40°.

The author, following Ramsay and Young's suggestion, found that enveloping of the bulb of the thermometer with cotton-wool made no appreciable difference in the readings. As a result, he continues to maintain that the received definition of the boiling point of a liquid is incorrect (comp. Abstr., 1884, 951). V. H. V.

Relation between the Absolute Boiling Points and Specific Volumes of Liquids. By J. A. Groshans (*Ber.*, **19**, 974—978).—The author in continuation of his observations on the law of density numbers (comp. this vol., pp. 194, 411, and 498), points out that if the values for $T\frac{n}{M}$ and of $v_s\frac{n}{M}$ are the same for any liquids, then the same volume of these liquids will yield the same volume of vapour v_t at the boiling point. The instances cited are propyl ether, ethyl valerate, and ethyl succinate. But $v_t = 81{\cdot}78\frac{T}{v_s}\left(81{\cdot}78 = \frac{22327}{273}\right)$, *i.e.*, the volume of 2 grams of hydrogen under standard conditions of pressure and absolute temperature; if then for T be substituted $P\frac{M}{n}$ and for v_s, $Q\frac{M}{n}$ (comp. p. 195); then $\frac{v_t}{v'_t} = \frac{P}{Q} \times \frac{Q'}{P'}$; in the particular case in which P = P′ and Q=Q′; then $\frac{v_t}{v'_t}$, or expressed in another form as $d_s = \frac{v_s}{M}$, then $\frac{d_s}{d'_s} = \frac{n}{n'}$. This equality of volume of vapour from equal volume of liquid can be predicted from the law of density numbers.

It is further shown that in the case of analogous monosubstituted derivatives of the hydrocarbons, for instance, the monohalogen-derivatives of benzene, the numerical values for $T\frac{n}{M}$ and $v\frac{n}{M}$ are the same; hence equal volumes of these liquids will give equal

volumes of vapour at the boiling points. Conversely, the values of the density numbers of the halogens are directly calculable from the values of v_t. So also for every halogen-atom introduced into the molecule the values for the constants $T\frac{n}{M}$ and $v_s\frac{n}{M}$ increase in arithmetical progression. V. H. V.

Deviations of Oxygen at Low Pressure from Boyle's Law. By C. Bohr (*Ann. Phys. Chem.* [2], **27**, 459—479).—The experiments of Regnault, Mendeléeff, and others, have shown that Boyle's law is not rigidly exact for air-pressures much below that of one atmosphere, although on the other hand, Amagat's results indicate that the variations at low pressures are too small and irregular to be of any account (Abstr., 1882, 1269). In this paper, a series of experiments with oxygen are described under pressures varying from 15 to 0·01 mm. at temperatures 11—14°; the possible sources of experimental errors are discussed in full, and shown to be inadequate to explain the observed variations from the law, even when all are in the same direction.

The results of the experiments seem to indicate that under these conditions the law is not expressible by the simple formula $pv = k$, but rather by a formula $(p + \alpha)v = k$, in which α is a constant within certain limits of pressure. Thus at pressures above 0·70 mm. value for α is 0·109, whilst below 0·7, this value is 0·07. Thus oxygen seems to undergo a change of aggregation at that limit. V. H. V.

Lecture Experiment on Gaseous Diffusion. By A. Winkelmann (*Ann. Phys. Chem.* [2], **27**, 479—480).—In experiments on the vapour-tension of liquids in gases contained over mercury, it has frequently been observed that the mercury column attains its final level only after a certain interval of time. It is proposed to illustrate the phenomenon of diffusion by observing the difference of level of mercury after a certain time in two tubes placed side by side, containing air and hydrogen respectively, and into which a quantity of ether more than sufficient to saturate the volume of contained gas has been introduced, the initial level of mercury being the same in both tubes. V. H. V.

Catalytic Action of Glass. By W. Alexéef (*Ber.*, **19**, 812).—A reply to Menschutkin and Konowalow (this vol., p. 299).

Gravitation and Atomic Weight. By L. Dulk (*Ber.*, **19**, 932—942).—In this paper, an attempt is made to refer the atomic weight of the elements to the laws of gravitation, that is to say, that the atoms attract one another with a force directly proportional to their masses and inversely proportional to the square of their distances, it being presupposed that the atoms do not consist of different quantities of matter of the same kind, but that each chemically different atom consists of matter of its peculiar kind, namely, a peculiar aggregation of the cosmical ether. If, then, the atoms be represented as circles it is shown that certain ratios between the squares of the radii of two or

more circles (whose circumferences touch one another, and which are inscribed within another circle, representing hydrogen, whose radius is taken as unity), correspond with differences of successive members of the same family of elements or corresponding members of different families. Thus to take the example of the alkali metals, the atomic weight of the element lithium would be represented by two such circles of radius $\frac{1}{2}$, and its atomic weight is equal to $2\frac{1}{r^2} - 1 = 7$, while those of sodium, potassium, rubidium, and cæsium are deducible from a general formula $2\frac{1}{r^2} + \frac{1}{r^2}\frac{1}{\rho^2}$, in which the values for r are successively $\frac{1}{3}, \frac{1}{4}, \frac{1}{6}$, and $\frac{1}{3 \times 3 \times \frac{3}{2}}$, and for ρ, $\frac{4}{3}, \frac{6}{4}, \frac{10}{6}$, and $\frac{13}{7{\cdot}5}$. Thus the ratio of the atomic weights can be represented by geometrical figures, a series of which are given in the original paper. According to such a theory, the molecular impacts would be conditioned by the rotation of the atoms and molecules, and also such relations as those of elasticity and friction could easily be deduced. The author, however, allows that in this theory the atoms are represented in terms of one dimension, whereas it is probable that they should be more correctly represented in terms of three dimensions. V. H. V.

Filtering Apparatus. By O. N. Witt (*Ber.*, **19**, 918—919).—It is proposed to replace the platinum perforated cone by perforated plates with sloping edges, made of glass or more conveniently of porcelain. For filtration these are covered with two or more layers of thick filter-paper, which are caused to adhere firmly to the upper surface by the pressure of the suction pump. This apparatus is very convenient for the filtration and purification of crystalline substances. V. H. V.

Inorganic Chemistry.

Purification of Bromine. By J. S. Stas (*Zeit. anal. Chem.*, **25**, 213).—The bromine is dissolved in potassium bromide and distilled with the addition of zinc oxide. The potassium retains the chlorine and the zinc the iodine. M. J. S.

Action of Red Hot Platinum on Phosphorus Fluorides. By H. Moissan (*Compt. rend.*, **102**, 763—766).—When platinum is heated to redness in contact with phosphorus trifluoride, the gas is completely absorbed and the platinum melts more or less completely owing to the formation of platinum phosphide and fluoride. If a rapid current of the gas is passed through a heated platinum tube containing spongy

platinum the issuing gas contains a small quantity of phosphorus pentafluoride, formed doubtless by the action of liberated fluorine on the excess of trifluoride. Moreover, if the issuing gas is passed into a mixture of potassium iodide and starch, a deep blue coloration is instantly produced, and if it is passed into a solution of potassium iodide, sufficient iodine is liberated to impart a strong coloration to chloroform. The gas also attacks mercury, and if collected in a carefully dried bulb it slowly attacks the glass with formation of silicon fluoride.

A mixture of phosphorus trifluoride and pentafluoride gives no immediate coloration with potassium iodide and starch, although both fluorides liberate iodine slowly, and it would seem from the above results that a small quantity of fluorine is liberated. Further experiments are however required to establish this fact, since the blue coloration is so readily produced by many substances.

If phosphorous pentafluoride is passed over red-hot platinum a similar decomposition takes place, but the action of the issuing gas on potassium iodide is still more strongly marked. C. H. B.

Solubility of Sulphur in Alcohol. By A. G. Bloxam (*Chem. News*, **53**, 181).—Sulphur is deposited in white prisms from its solution in hot alcohol. The crystals, at first transparent, within 36 hours change into octahedra and become opaque and yellow. It is important to note this fact when using vulcanised india-rubber corks in the presence of alcohol. D. A. L.

Decomposition of Hypophosphoric Acid. By A. Joly (*Compt. rend.*, **102**, 760—763).—When the normal hydrate, $P_2O_4,2H_2O$, is heated at 70° in a water-bath, it melts suddenly and decomposes with considerable development of heat into a mixture of phosphorous and metaphosphoric acids. If the product is dissolved in water, the metaphosphoric acid is almost immediately converted into orthophosphoric acid.

The decomposition of the hypophosphoric acid is not complete unless it is maintained for some minutes at 70°, or better if the temperature is gradually raised to 100°. If the product is heated to about 120°, it becomes turbid, bubbles of spontaneously inflammable gas are given off, and an orange-yellow precipitate is formed and rapidly spreads throughout the whole mass. If the residue is dissolved in water and the solution neutralised, it gives a white precipitate with silver nitrate, which rapidly becomes brown owing to the presence of a small quantity of undecomposed phosphorous acid. The orange-yellow product has all the properties of solid hydrogen phosphide. It is evident that the decomposition of the mixture of phosphorous and metaphosphoric acids takes place differently from that of pure phosphorous acid. At the comparatively low temperature at which decomposition takes place, the metaphosphoric acid acts as a dehydrating agent, and the products are pyrophosphoric acid and liquid hydrogen phosphide, the latter immediately splitting up into the gaseous and solid hydrogen phosphides. C. H. B.

Carbonic Anhydride in the Atmosphere. By E. Wollny (*Bied. Centr.*, 1886, 217—224).—Saussure, Boussingault, and others have estimated the amount of carbon dioxide contained in the air at from 2 to 6 vols. per 10,000.

Schlössing thinks that this regularity in the quantity is due to the action of the calcium salts contained in the waters of the ocean, carbonates and bicarbonates being alternately formed as the quantity of carbon dioxide in the air is larger or smaller. Reiset, who has given great attention to the subject, does not find the quantity so high nor the fluctuations so great, his estimate being from 2·82 to 3·16 vols. per 10,000.

In the present paper, the author collects and compares the observations of many observers, and comes to the conclusion that the quantity is not nearly so regular as has been asserted, but that on the contrary it varies within very wide limits. As the cause of such differences, he attaches great importance to the combustion of carbonaceous materials in various industrial processes; the breathing of man and animals he does not consider important, it being a constant and regular quantity. The soil, on the contrary, he believes to be an abundant source of carbon dioxide owing to the constant and rapid decay of organic matter, the soil becomes overcharged and it escapes into the air, more freely from fallow and tilled ground than from pasture. As absorbents of the excess, the author considers the quantity assimilated by plants to be the most important, after which he places sea-water, the action of which he regards as very potent.

J. F.

Decomposition of Potassium Chlorate by Heat. By E. J. Maumené (*Chem. News*, **53**, 145—147).—It is remarkable that the equation proposed by Teed (Proc., 1885, p. 105) for the decomposition of potassium chlorate by heat is approximately the same as that given by the author 13 years ago, although obtained in a somewhat different manner.

D. A. L.

Crystallised Hydrated Barium Silicate. By A. Cossa and G. La Valle (*Zeit. Kryst. Min.*, **11**, 399—400).—On the sides of a glass vessel containing baryta-water and closed for 27 years, transparent, columnar crystals were formed. An analysis gave—

SiO_2.	BaO.	H_2O.	Total.
18·56	48·23	33·33	100·12

The crystals are rhombic; axial ratio, $a : b : c = 0·8838 : 1 : 0·3772$; observed forms, $\infty\breve{P}3$, $\bar{P}\infty$, $2\bar{P}\infty$, $\infty\bar{P}\infty$.

B. H. B.

Behaviour of Plumbiferous Zinc on Remelting. By K. Kraut (*Zeit. anal. Chem.*, **25**, 169—172).—On allowing plumbiferous zinc to remain at rest after fusion, the lead concentrates itself in the lower part. Thus, after fusing 2 kilos. of zinc containing 1·656 per cent. of lead, the lowest part (45 grams) was found to contain 5·339 per cent., and the highest part 1·003 per cent. of lead. By five subsequent fusions of the same sample, removing on each occasion

the lower portions, the percentage in the uppermost layer was reduced to 0·561. On this account the analysis of selected sheets is no guide to the mean composition of a lot, even from a single crucible charge: sampling by granulating is quite useless, unless the whole charge is vigorously stirred just before, and the entire sample removed is employed for the analysis. M. J. S.

Action of Nitric Acid on Mercuric Sulphide. By J. L. Howe (*Amer. Chem. J.*, **8**, 75).—Mercuric sulphide is not changed by boiling with pure nitric acid (sp. gr. 1·42); the addition of one drop of dilute hydrochloric acid, however, causes the conversion of the sulphide into a yellowish-white compound, presumably $Hg(NO_3)_2,2HgS$; the further addition of 10 drops of hydrochloric acid causes the complete solution of the yellowish compound. The same changes are brought about by dilute nitric acid containing a little hydrochloric acid as impurity. H. B.

Cerium Tungstates and Chlorotungstates. By P. Didier (*Compt. rend.*, **102**, 823—825).—When equal parts of normal sodium tungstate and anhydrous cerium chloride are heated, with or without fusion, in an inert atmosphere, channelled yellow crystals are obtained, which act strongly on polarised light, and have the composition $3(CeO,WO_3) + CeCl$.* If the cerium chloride is in excess, yellow on red hexagonal tables of the composition, $3(Ce_3O_2Cl),2WO_3$, are formed. Similar crystals were described, but not analysed by Radominski. They may also be prepared by passing hydrogen chloride over strongly heated cerosoceric oxide and tungstic anhydride.

If cerosoceric oxide is added in successive small portions to fused sodium paratungstate, the latter being kept in excess, the normal tungstate, CeO,WO_3, is obtained in minute, yellow octahedrons, resembling those of scheelite. Larger and more brilliant octahedra are obtained by fusing precipitated cerous tungstate with sodium chloride out of contact with the air. A double tungstate, $NaO,WO_3 + CeO,WO_3$, is obtained in octahedra resembling those of sulphur, by dissolving precipitated cerium tungstate in normal sodium tungstate.

Similar experiments with normal sodium molybdate and cerous chloride, and the acid molybdate and cerosoceric oxide, yield the normal molybdate CeO,MoO_3 in yellow crystals, which become green or blackish in contact with reducing gases.

Cerium molybdate and cerium tungstate seem to have the same form as scheelite. Cossa has already shown that didymium tungstate and didymium molybdate are isomorphous with the corresponding calcium and lead salts.

Cerium chloromolybdate has not yet been obtained.

C. H. B.

A Monosymmetrical Sodium-alum. By C. Soret (*Zeit. Kryst. Min.*, **11**, 434—435).—The crystals were formed at 8° to 12° from a concentrated solution of sodium alum which was covered with abso-

* The formulæ are given as in the original paper, Ce = 47.—C. H. B.

lute alcohol, at the contact of the two liquids. Analysis gave the following results :—

SO_3.	Al_2O_3.	Na_2O.	H_2O.	Total.	Sp. gr.
35·59	11·40	7·12	46·75	100·86	1·73

The crystals were monosymmetrical; $a : b : c = 2·5060 : 1 : 0·9125$; $\beta = 70° 59'$. B. H. B.

Atomic Weights of Cobalt and Nickel. By C. Zimmermann (*Annalen*, **232**, 324—347).—The oxide of cobalt used in these determinations is purified by the following process :—Silica and the metals of the copper and arsenic groups are removed in the usual way. Freshly precipitated mercuric oxide is brought into the cold solution. The iron in the solution is oxidised to ferric salt, and is then completely precipitated, together with a small portion of the cobalt by the addition of freshly precipitated mercuric oxide. The nickel may be precipitated by potassium cyanide and bromine-water from the alkaline solution. The potassium cobalticyanide is decomposed by evaporation with strong sulphuric acid. The residue is dissolved in water, and boiled with sodium chloride and mercuric oxide to precipitate the cobalt. The cobalt may also be precipitated as mercuric cobalticyanide, which on ignition leaves the cobalt in the form of oxide. A second method of separating the cobalt and nickel is to precipitate the cobalt by a mixture of sodium nitrite and potassium chloride. The precipitate is washed with potassium acetate and decomposed by sulphuric acid. The cobalt is deposited from the solution by electrolysis. The metal is dissolved in hydrochloric acid and precipitated as Co_3O_4 by mercuric oxide.

Cobalt monoxide is formed by igniting the higher oxides in an atmosphere of an indifferent gas. It is a non-magnetic pale-brown powder. It is perfectly stable at the ordinary temperature, but oxidises when heated in the air. The oxide is insoluble in ammonia, but dissolves in hydrochloric, nitric, sulphuric, acetic, tartaric, and perchloric acids, also in fixed alkalis, ammonium chloride, and ammonium thiocyanate.

The monoxide is converted into cobalticobaltous oxide, Co_3O_4, by ignition in the air. The atomic weight of the metal determined by this method is 58·74.

The oxide used in the determination of the atomic weight of nickel is purified as follows :—After removing silica and the metals of the copper and arsenic groups from the commercial oxide in the usual way, the cobalt is precipitated by means of potassium nitrite. The filtrate is treated with bromine-water for 24 hours to precipitate the manganese. The solution is then evaporated to dryness. The residue is dissolved in water, and the iron precipitated from the cold solution by mercuric oxide. The nickel is then thrown down by boiling the filtrate with sodium chloride and mercuric oxide, and is washed and ignited. Another method is to deposit the nickel electrolytically, after having removed copper and cobalt from the solution. The product is purified by solution in acid and reprecipitation with mercuric oxide.

Nickel monoxide has a pale-green colour. It is not magnetic. It is insoluble in acetic acid and in cold perchloric acid, neither is it attacked by solutions of ammonium chloride, ammonium thiocyanate, nor by sodium hydroxide. Nickel monoxide, prepared by igniting the hydroxide in the air, contains trace of the sesquioxide. The atomic weight of the metal, as determined by reducing the monoxide in hydrogen, is 58·56.

The atomic weights of nickel and cobalt are not identical.

W. C. W.

Conversion of Chromous Chloride into Chromic Chloride: Molecular States of Chromic Oxide. By Recoura (*Compt. rend.*, **102**, 865—869).—The author has redetermined the heat of conversion of chromous chloride into chromic chloride (Abstr., 1886, 1102), with the following results :—

Cr_2Cl_4 diss. + Cl_2 gas = Cr_2Cl_6, green, diss., develops + 102·8 cal.
Cr_2Cl_4 „ + Cl_2 gas = Cr_2Cl_6, grey, „ „ + 121·6 „

Chromic oxide exists in three different molecular conditions. The first is obtained by precipitating a solution of either variety of chromic chloride (this vol., p. 508), or of any violet chromium salt with an equivalent quantity of soda. If treated with hydrochloric acid immediately after precipitation, it combines with 6 mols. of acid with development of + 41·4 cal.

The second variety is obtained by precipitating the oxychloride Cr_2Cl_4O with 4 mols. sodium hydroxide. Immediately after precipitation, it combines with 4 mols. of hydrochloric acid only, with development of + 24·2 cal. The subsequent addition of a further quantity of 2 mols. of acid produces no thermal disturbance.

The third form is obtained when either of the preceding varieties is dissolved in the necessary excess of soda (18 mols. in the first case, 6 mols. in the second), and reprecipitated by neutralising the excess of alkali. It combines with only 4 mols. of hydrochloric acid, with development of + 20·0 cal.

C. H. B.

Titration of Acid Tungstates. By H. Schmidt (*Amer Chem. J.*, **8**, 16—22).—The object of the investigation was to ascertain whether an acid tungstate might not be used as an agent for standardising an alkaline solution; but as the results varied with the temperature and the time, the method is valueless.

Taking the salt $12WO_3,5Na_2O + 28H_2O$, and using phenolphthaleïn or aurin as the indicator, it was found that as a mean of all experiments 14·03 per cent. of sodium oxide was required for neutralisation, which agrees with the above formula of Gibbs.

H. B.

Paratungstates. By G. v. Knorre (*Ber.*, **19**, 819—827).—The author has prepared a number of double salts of paratungstic acid in the hope of determining whether salts of this acid have the general formula $3R_2O : 7WO_3$ or $5R_2O : 12WO_3$. The salts $Na_2Am_4W_7O_{24} + 9H_2O$ and $Na_2Am_8W_{12}O_{41} + 13H_2O$ have already been described by Lotz (*Annalen*, **91**, 56) and others. By mixing boiling solutions of

sodium paratungstate (1 mol.), and zinc sulphate (2 mols.), the salt $Na_2Zn_2W_7O_{24} + 15$ aq. (slightly soluble in boiling water) was obtained. If the mixture is made below 60°, the salt contains $21H_2O$. When solutions of equal molecular proportions of sodium paratungstate and cadmium sulphate are mixed at 80°, a white crystalline salt $Na_2Cd_2W_7O_{24} + 18H_2O$ separates out. Lotz has described a salt to which he ascribed the formula $3[\frac{1}{5}(NH_4)_2O,\frac{4}{5}CdO]7WO_3 + 7H_2O$. When solutions of equal molecular proportions of sodium tungstate and magnesium sulphate are mixed at 70°, the salt $Na_6W_7O_{24},Mg_3W_7O_{24} + 33H_2O$ is formed. If more than 3 mols. sulphate are added to 1 of tungstate, the salt $Mg_3W_7O_{24} + 24H_2O$ separates in the form of a white crystalline salt. Lotz has described a salt $(NH_4)_2Mg_2W_7O_{24} + 10H_2O$, and Marignac one of the formula $(NH_4)_4Mg_3W_{12}O_{41} + 24H_2O$. By mixing solutions of equal proportions of sodium tungstate and manganese sulphate at 70°, the salt $Na_6W_7O_{24},Mn_3W_7O_{24} + 36H_2O$ was obtained as a pale-yellow, crystalline compound. Similarly a greenish, crystalline salt, $Na_6W_7O_{24},Cu_3W_7O_{24} + 32H_2O$, was obtained, but when an excess of cupric sulphate was employed the salt $Cu_3W_7O_{24} + 19H_2O$ separated as a pale blue precipitate.

Reviewing these results, and those hitherto obtained by other investigators, the author is unable to decide whether in paratungstates the relationship of base to acid is 3 : 7 or 5 : 12, or whether possibly modifications exist corresponding with each of these ratios.

L. T. T.

Uranium. Part III. By C. Zimmermann (*Annalen*, **232**, 273—324).—The black and the olive-coloured oxides of uranium (U_2O_5 and U_3O_8) described by Péligot (*Ann. Chim. Phys.*, [3], **5**), have been investigated by Wertheim (*J. pr. Chem.* **29**, 211), Ebelmen (*Annalen*, **43**, 295), Rammelsberg (*Ann. Phys. Chem.* **59**, 1), Drenckmann (*Zeitschrift gesammt Naturwissens.*, **17**, 113), and Bemelé (*Ann. Phys. Chem.* **124**, 125), who obtained contradictory results regarding the existence of these two oxides. The author finds that Péligot's black oxide is merely a mixture of U_3O_8 and UO_2, of varying composition. When uranium dioxide is heated in an atmosphere of oxygen until its weight becomes constant, U_3O_8 is formed. The colour of this oxide varies from green to black, but it always leaves a green mark on unglazed porcelain. The oxide remains unchanged when it is ignited and allowed to cool in oxygen, but it loses a small quantity of oxygen if it is heated in the air and rapidly cooled in an atmosphere of nitrogen. Ignition in an indifferent gas completely converts the uranosouranic oxide to uranium dioxide.

The atomic weight of uranium was determined by converting the dioxide into the uranosouranic oxide, U_3O_8, by ignition in oxygen. The dioxide used in the experiments was prepared from the oxalate, from the tetroxide, by ignition of uranyl nitrate, and from U_3O_8 prepared by precipitation with mercuric oxide. The mean of 10 experiments, in each of which from 5·708 to 15·8996 grams of UO_2 were used, gives 239·02 as the atomic weight of uranium. The atomic weight was also determined by converting sodium uranyl acetate into sodium uranate U = 238·9. The author finds that the tetroxide $UO_4 + 2H_2O$, described by Fairley (this Journ., 1877, i, 127) is very hygro-

scopic, and that it begins to decompose at 115°. The existence of a definite hydrate containing 4 mols. H_2O, $UO_4 + 4H_2O$, is denied.

W. C. W.

Reaction of Tin with Sulphuric and Nitric Acids. By H. Bassett (*Chem. News*, **53**, 172).—A mixture of 1 part of sulphuric acid, 2 parts of nitric acid, and 3 parts of water, all by measure, dissolves tin in the cold, with the evolution of nearly pure nitrous oxide, producing at the same time a clear solution of stannic sulphate. If, however, the temperature has been allowed to rise, the solution becomes opalescent, and on heating in a water-oven for an hour, it becomes nearly solid and opaque. When the solution, containing nitric acid, is poured into boiling water, the whole of the tin is precipitated as metastannic acid. Attempts have been made to apply this reaction to the analysis of tin alloys, but as yet without success.

D. A. L.

Combination of Vanadic Anhydride with Oxy-acids. By A. Ditte (*Compt. rend.*, **102**, 757—759).—Vanadic anhydride dissolves in warm concentrated sulphuric acid, and the solution deposits small, lemon-yellow crystals of the composition $V_2O_5,3SO_3 + 3H_2O$. These crystals are very hygroscopic, and dissolve readily in dilute sulphuric acid, forming a pale green liquid which is simply a solution of vanadic acid. If the solution is heated alone, it deposits vanadic anhydride, but if it is mixed with sulphuric acid and concentrated, the double compound is deposited in brilliant, transparent, orange-red crystals which have the same composition as the lemon-yellow crystals.

When vanadic anhydride is heated with a concentrated solution of phosphoric acid, it is converted into golden-yellow plates of the composition $V_2O_5,P_2O_5 + 14H_2O$, very slightly soluble in concentrated solutions of phosphoric acid, but readily soluble in dilute solutions. When the crystals are gently heated, they lose $10H_2O$, but retain their shape and appearance. If the solution of phosphoric acid is more concentrated, or if soluble vanadic anhydride is left in contact with a moderately concentrated solution of phosphoric acid, brilliant, yellowish-green plates are obtained, which, when dried at 100°, have the composition $2V_2O_5,3P_2O_5 + 9H_2O$.

When a warm concentrated solution of arsenic acid is poured into a red solution of vanadic acid, a precipitate is produced which dissolves in excess of arsenic acid, forming a pale yellow solution which becomes deeper in colour, and eventually red as more vanadic acid is added. When the liquid cools, it deposits brilliant yellow crystals of the composition $V_2O_5,As_2O_5 + 18H_2O$. If vanadic anhydride is mixed with a warm concentrated solution of arsenic acid, it is converted into crystalline plates which are only slightly soluble in the concentrated liquid, but dissolve readily on adding water. The solution has a garnet-red colour, and deposits crystals similar to the preceding compound, but containing only $14H_2O$.

Vanadic anhydride or acid, when heated with a concentrated solution of iodic acid, is rapidly converted into brilliant nacreous plates which have the composition $V_2O_5,I_2O_5 + 5H_2O$, and are very slightly soluble in the liquid in which they are formed. The crystals

lose $4H_2O$ at 150°, become yellow at a bright red heat, and if more strongly heated give off iodine and oxygen, vanadic anhydride being left. The mother-liquor from these crystals, if concentrated and allowed to stand, yields golden-yellow, nacreous plates of the composition $2V_2O_5,3I_2O_5 + 18H_2O$.

If ammonium vanadomolybdate, which will be described subsequently, is boiled with aqua regia containing an excess of nitric acid, a reddish, non-crystalline deposit is obtained, and if this is boiled with a large excess of nitric acid, it gradually changes into small, slender, transparent, orange-red needles of the composition $V_2O_5,8MO_3 + 5H_2O$. Vanadomolybdic acid is only slightly soluble in boiling nitric acid, and is still less soluble in water. In this respect, it differs from phosphomolybdic and arsenomolybdic acids, which are readily soluble in water.

Vanadic acid also combines with tungstic, silicic, oxalic, tartaric, and other acids. C. H. B.

Mineralogical Chemistry.

Apatite from Turkestan. By P. v. Jeremèeff and P. D. Nikolaieff (*Zeit. Kryst. Min.*, **11**, 389—392).—The apatite crystals described were found in a sandy clay on the banks of the Maidan-tal river. The measurements of the crystals lead to the axial ratio $a : c = 1 : 0{\cdot}7345151$. The analysis gave—

Insoluble residue.	Cl.	F.	P_2O_5.	CaO.	MnO.	Fe.	Total.	Sp. gr.
0·12	trace	3·64	41·93	55·29	0·18	trace	101·16	3·199

The Turkestan apatite is consequently a pure fluorine-apatite with the formula $3Ca_3(PO_4)_2,CaF_2$. B. H. B.

Minerals from Vesuvius. By E. Scacchi (*Zeit. Kryst. Min.*, **11**, 404—405).—*Euchlorine*, a mineral found by A. Scacchi in 1869, forms thin crusts on lava. An analysis of the crystals, dissolved in hydrochloric acid, gave—

SO_3.	CuO.	K_2O.	Na_2O.	Total.
43·98	41·50	8·04	6·48	100·00

Formula: $(KNa)_2Cu_3S_3O_{13}$. The mineral is rhombic; $a : b : c = 0{\cdot}7616 : 1 : 1{\cdot}8755$.

Another pale-blue sublimation product, named "*ericalco*," by A. Scacchi, is soluble in water, and contains 51·92 per cent. of chlorine, and 48·08 per cent. of copper.

A third sublimation product, "*melanotallo*," gave on analysis—

$CuCl_2$.	CuO.	H_2O (at 100°).	Total.
57·37	31·39	11·24	100·00

B. H. B.

Hæmafibrite and Hæmatolite. By E. Bertrand (*Jahrb. f. Min.*, 1886, **1**, Ref., 12—13).—These minerals were discovered at the Nordmark manganese mine, Wermland, Sweden.

Hæmatolite crystallises in the monoclinic system. Analysis gave—

As_2O_5.	MnO.	FeO.	MgO.	CaO.	H_2O.	Total.
25·70	34·55	13·95	8·10	2·52	16·08	100·90

Formula: $2(3MnO,As_2O_5),8(MnO,H_2O) + 6H_2O$.

Hæmafibrite (comp. Abstr., 1885, 959) is rhombic. Analysis gave the following results:—

As_2O_5.	MnO.	FeO.	MgO.	CaO.	H_2O.	Total.
29·94	46·98	4·65	2·00	1·50	14·93	100·00

Formula: $2(3MnO,As_2O_5),7(MnO,H_2O)6H_2O$. B. H. B.

Minerals from Oberwiesenthal. By A. Sauer (*Zeit. Kryst. Min.*, **11**, 412—414).—In the nepheline-basalt of the Oberwiesenthal eruptive mass, Saxony, there occur augite, hauyne, titaniferous mica, hornblende, peroffskite, leucite, and pseudomorphs of analcime after leucite. In the phonolite is found sanidine, augite, hauyne, melanite, and hornblende. In the leucitophyre, pseudomorphs of sanidine and mica after leucite are found. B. H. B.

Analyses of Garnet and Analcime. By P. Nikolaieff (*Zeit. Kryst. Min.*, **11**, 392).—*Garnet.*—I, compact garnet from the Isset river; II, demantoïd from Teljanskij Kljutsch:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Ignition.	Total.	Sp. gr.
I.	38·60	24·18	trace	—	35·03	0·97	1·18	99·96	3·482
II.	35·33	2·22	30·44	0·27	31·52	trace	—	99·78	3·847

Analcime (cuboite) from Blagodat; I, crystalline; II, compact:—

	H_2O.	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Na_2O.
I.	8·13	54·42	22·89	0·40	0·87	trace	13·00
II.	5·01	55·28	21·21	0·93	3·70	0·39	8·93

	K_2O.	Total.	Sp. gr.	
I.	—	99·71	2·277	
II.	2·73	98·18	2·481	B. H. B.

Idocrase. By A. Cossa (*Zeit. Kryst. Min.*, **11**, 408).—In the mountains above Almeze and Condove, idocrase crystals occur planted on compact bornite. Analysis gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	H_2O.	Total.	Sp. gr.
37·46	15·51	5·39	35·98	1·97	3·40	99·71	3·39

B. H. B.

Artificial Physical Changes in the Felspars of Pantelleria. By H. Förstner (*Jahrb. f. Min.*, 1886, **1**, Ref., 5—7).—The author

has shown that on heating the axial angle of a plagioclase of Cuddia Mida approaches that of the sodium orthoclase that chemically and crystallographically most closely resembles it. He now shows the formation of twin crystals, and change of system at high temperatures in the sodium microline and sodium orthoclase from Pantelleria. Analogous changes are produced by pressure (comp. Abstr., 1884, 1104). B. H. B.

Minerals from the Krakatoa Ashes. By J. W. Retgers (*Zeit. Kryst. Min.*, **11**, 415—419).—1. *Felspars.*—The greater portion of the felspars in the Krakatoa ashes fallen at Buitenzorg consisted of plagioclase, with a very small quantity of sanidine. By means of potassium mercury iodide solution, the felspars were divided into 21 groups of different specific gravity. The analysis of all the felspars gave the following results:—

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	Total.
58·29	27·19	8·27	5·82	1·22	100·79

From his investigations, the author concludes that at a given temperature basic felspars separate out from a molten glass of the composition of the Krakatoa ashes, and at a lower temperature and from an acid magma, acid felspars separate out, and consequently all the plagioclases from pure albite to pure anorthite are present. This the author regards as a new confirmation of Tschermak's theory.

2. *Hypersthene.*—Analysis gave—

SiO_2.	TiO_2.	Al_2O_3.	FeO.	MnO.	CaO.	MgO.	Total.
52·3	trace	6·1	27·7	trace	2·2	13·6	101·9

The following forms were observed: P, $2\bar{P}2$, $\infty\bar{P}\infty$, $\bar{P}2$, ∞P, $\infty\breve{P}\infty$.

3. *Augite.*—Analysis gave—

SiO_2.	TiO_2.	Al_2O_3.	FeO.	MnO.	CaO.	MgO.	Total.
48·6	trace	8·2	14·0	trace	18·9	11·6	101·3

The forms observed were: + P, 0P, − P, ∞P, −2P, $\infty\breve{P}\infty$, + 2P, $\infty\breve{P}\infty$.

4. In addition to the above-named minerals, magnetite occurs in small octahedra (with 6·73 per cent. of TiO_2), and non-magnetic titaniferous iron, and small colourless hexagonal columns of apatite. Iron pyrites, magnetic pyrites, and anhydrite are mentioned as foreign constituents of the ashes (comp. Abstr., 1884, 974, 975).

B. H. B.

Analyses of Minerals from the Basalt of Iceland. By R. Bréon (*Zeit. Kryst. Min.*, **11**, 414—415).—I. Labradorite from the basalt of Stigahlid; II. Labradorite from the basalt dyke between Bolungarvick and Huifsdalr; III. Labradorite from the basalt of Skagastrond; IV. Anorthite from the basalt of Stigahlid:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	Total.
I.	53·49	26·02	4·63	11·14	1·18	1·09	3·22	100·77
II.	51·90	29·16	2·22	11·17	0·61	0·43	3·22	98·71
III.	53·60	27·75	1·14	10·87	0·40	0·19	4·33	98·28
IV.	46·80	33·50	1·60	18·00	0·40	0·30	0·70	101·30

B. H. B.

Topaz and Tourmaline from Tasmania. By A. v. Groddeck (*Zeit. Kryst. Min.*, **11**, 440—441).—A rock from Mt. Bischoff in Tasmania, in appearance resembling a quartz porphyry, proved to be a porphyritic topaz rock, the ground-mass of which consisted of 35 per cent. of topaz and 65 per cent. of quartz. The occurrence of tin ore at Mt. Bischoff is confined to peculiar mineral masses of this kind. An analysis of a white mass gave the following results:—

SiO_2.	Al_2O_3.	CaO.	F.	Total.	Sp. gr.
33·24	57·02	0·83	17·64	108·73	3·456

The mineral is consequently compact topaz. The greyish-blue mineral associated with this is compact tourmaline, as is shown by the following analysis:—

SiO_2.	Al_2O_3.	B_2O_3.	FeO.	MnO.	CaO.	MgO.
36·86	36·72	10·56	5·66	0·66	0·34	3·92

K_2O.	Na_2O.	H_2O.	F.	Total.	Sp. gr.
1·11	3·57	1·16	0·61	101·17	3·042

B. H. B.

Crocydolite and Fibrous Quartz from the Cape. By A. Renard and C. Klement (*Zeit. Kryst. Min.*, **11**, 442—443).—An analysis of crocydolite from the Orange River gave the following results:—

SiO_2.	Fe_2O_3.	FeO.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
51·89	19·22	17·53	0·40	2·43	7·71	0·15	2·36	101·69

At the Cape, two varieties of fibrous quartz also occur: I, the well-known brown variety (tiger's-eye), and II, a darker variety of a bluish or greenish colour. The analyses gave—

	SiO_2.	Fe_2O_3.	FeO.	Al_2O_3.	CaO.	MgO.	H_2O.	Total.
I.	93·05	4·94	—	0·66	0·44	0·26	0·76	100·11
II.	93·43	2·41	1·43	0·23	0·13	0·22	0·82	98·67

The microscopic examination shows that this fibrous quartz is not a pseudomorph after crocydolite, as has hitherto been supposed, but has been formed by infiltration of quartz between the fibres.

B. H. B.

The so-called Liparites and Sanidophyres from the Siebengebirge. By A. v. Lasaulx (*Jahrb. f. Min.*, **1**, 1886, Ref., 55).—The grey variety of liparite from the Rosenau in the Siebengebirge contains neither quartz nor acid glass, but is impregnated with chalcedony. A new microscopic investigation shows that the felspars

occur only in angular fragments, whilst the ground-mass consists of an intimate mixture of chalcedony and opal. The author therefore regards the rock as a fresh water quartzite containing breccia-like fragments of ordinary trachyte. The second variety of liparite from the same locality is a trachyte with mica, some hornblende, titanite, and zircon. The ground-mass contains 18·91 per cent. of opal and chalcedony. The rock is not liparite, but a trachyte impregnated with chalcedony and opal. B. H. B.

Organic Chemistry.

Action of Heat on Liquid Paraffins. By L. M. Norton and C. W. Andrews (*Amer. Chem. J.*, 8, 1—9).—The hydrocarbons examined, normal hexane, normal pentane, and isohexane, were obtained from petroleum and gasoline, by fractional distillation followed by treatment with bromine and with nitric acid. The hydrocarbons were slowly passed through a heated glass or porcelain tube; the results obtained are embodied in the following table:—

	Normal hexane		Isohexane	Normal pentane
	at a red heat.	at 700°.	at a red heat.	at a red heat.
Hexylene....	very small	very small	very small	traces?
Amylene	very small	very small	traces	
Butylene	none	small	moderate	
Propylene....	large	large	large	large.
Ethylene	large	none	large	large.
Butine	small	small	small	small.
Benzene	small	none	none	none.
Gases not absorbed by bromine....	large	moderate	large	large.

H. B.

Synthesis of Ammonium Cyanide by the Silent Discharge. By A. Figuier (*Compt. rend.*, **102**, 694—695).—When a mixture of 1 vol. methane and 2 vols. nitrogen is passed through a tube subjected to the influence of a silent discharge, ammonium cyanide is formed.

The gas issuing from the apparatus has an aromatic odour, which is due to the formation of condensed hydrocarbons, and is still more marked when pure methane is treated in the same way.

Methane is not dissociated by the action of the silent discharge, and it follows that the ammonium cyanide is formed by the direct combination of methane and nitrogen. C. H. B.

Alkali Platinocyanides. By T. Wilm (*Ber.*, **17**, 950—956).—Potassium platinochloride, or Gmelin's salt, can be obtained in various ways from ammonium or potassium platinochlorides and from platinous

and platinic chlorides. It appears to exist in several isomeric modifications, for frequently, with slight modifications in the method of preparation, crystals different in appearance, colour, and fluorescence are produced. The observations of Martius on the ready co-crystallisations of potassium and sodium platinocyanides are confirmed. Thus on treating ammonium platinochloride with soda and potassium cyanide, colourless, pyramidal crystals separate, which, under slightly varied conditions, change to an orange-yellow tint; it results from these experiments, as also from those of Martius, that the maximum tint is produced when the two double cyanides are mixed in equimolecular proportion; the greater the proportion of potassium to sodium salt, the more transparent are the crystals, and conversely the greater the proportion of the sodium salt, the more green and fluorescent, like uranium glass, are the crystals obtained. Potassium platinocyanide differs from potassium sodium platinocyanide in effloresing at ordinary temperatures and losing all its water of crystallisation at 120°, becoming of a pale golden colour, whilst the latter does not effloresce, but is rendered anhydrous at 120°, turning a pale yellow colour, which changes however to a red-brown tint on exposure to sunlight. The analysis of the potassium sodium platinocyanides points to a composition $K_2Pt(CN)_4,Na_2Pt(CN)_4 + 6H_2O$. V. H. V.

Halogen Additive Products of Potassium Platinocyanide. By T. Wilm (*Ber.*, **19**, 959—971).—Hadow has described (this Journal, 1860, 106) a chlorine additive product obtained by treating potassium platinocyanide with chlorine, and ascribed to it the composition $5K_2Pt(CN)_2 + K_2Pt(CN)_4Cl_2 + aq$. It is here shown that if potassium platinocyanide is treated with hydrochloric acid or the halogen elements, delicate, copper-red crystals of the composition $[K_2Pt(CN)_4 + 3H_2O]_3X$ separate out in the latter case, but in the former a compound $[K_2Pt(CN)_4,3H_2O]_3HCl$. These substances can be purified by recrystallisation from a small quantity of water and alcohol. Their aqueous solutions are colourless or nearly so; the crystals themselves effloresce with decomposition in the air; when heated at 120° they become anhydrous, changing from copper-red to dark blue-green. The halogen or hydrochloric acid is readily eliminated from them by alkalis or alkaline carbonates; they even liberate iodine from potassium iodide. The particular method adopted for their analysis is described in detail in the original paper. V. H. V.

Volatility of Oxynitriles. By L. Henry (*Compt. rend.*, **102**, 768—772).—*Acetoxyacetonitrile*, $C_4H_5NO_2$, is obtained by the action of monochloracetonitrile on an alcoholic solution of potassium acetate. It is a colourless liquid which boils at 175° under a pressure of 767 mm., and has an odour resembling that of acetic acid, and a sweetish bitter taste; sp. gr. at 13·5° = 1·1003. It dissolves somewhat easily in water, yields monochloracetic acid with hydrochloric acid, and differs very considerably from its isomeride ethyl cyanoformate both in chemical and in physical properties.

Acetoxypropionitrile is obtained by the action of acetic chloride on primary lactonitrile. With hydrochloric acid, it yields primary

chloropropionic acid, but in other respects it closely resembles its isomeride ethyl cyanacetate. Both are colourless, almost odourless liquids, insoluble in water, and both boil at about the same temperature under ordinary pressure; sp. gr. of ethyl cyanacetate at 13·5° = 1·0664; of acetoxypropionitrile at 13·5° + 1·0770.

A comparison of the boiling points of these compounds and their isomerides:—

	B. p.	
Ethyl cyanoformate, CN·COOEt	115°	Diff. + 93°
Ethyl cyanacetate, CN·CH_2·COOEt	208	
Acetoxyacetonitrile, CN·CH_2·AcO	175	Diff. + 30
Acetoxypropionitrile, CN·CH_2·CH_2·AcO .	205—208°	

confirms the author's previous results. The interposition of CH_2 in the chain CN·CO raises the boiling point more than 90°, whilst a similar interposition in the chain CN·CH_2 raises the boiling point only 30°. The presence of the chain CN·CO materially reduces the boiling point of a compound, but only when the two components are in direct union. If they are separated by CH_2, the normal volatility is restored.

C. H. B.

Preparation of Mercury Fulminate. By E. Beckmann (*Ber.*, **19**, 993—995).—Mercury fulminate is conveniently prepared by the following modification of Liebig's process: 50 grams of mercury are dissolved in 600 grams of nitric acid (sp. gr. 1·4); the solution is poured into a capacious flask and warmed at 25—30°; and 550 grams of alcohol (98·5 per cent.) at the same temperature is added. The alcohol must neither be added too quickly, otherwise mercury separates out, nor too slowly, or an explosion occurs. The thick white vapours evolved are best led through a wide tube, all contact with any flame being carefully avoided; when these have disappeared a litre of water is poured in, and the separated fulminate washed with water.

The hydroxylamine hydrochloride prepared from the fulminate by Carstanjen and Ehrenberg's process (compare Trans., 1884, 13) is best preserved in a bell-jar over quicklime; its decomposition with formation of ammonium chloride is thus prevented. V. H. V.

Chlorethers. By L. Godefroy (*Compt. rend.*, **102**, 869—872).—*Monochlorovinyl ethyl ether*, CHCl : CH·OEt, is obtained by the action of zinc-dust or the zinc-copper couple on the compound $C_6H_{12}Cl_2O_3$, prepared by passing chlorine through a mixture of potassium dichromate and alcohol. It is a colourless, mobile liquid with a sweet but penetrating odour, and is insoluble in water, but dissolves in alcohol and ether. It boils at 123° under normal pressure; sp. gr. at 19° = 1·0361; vapour-density 3·52. It absorbs bromine energetically with formation of the ether CHClBr·CHBr·OEt, a yellow liquid which boils at 170—180° with partial decomposition, and with chlorine it yields trichlorethyl ether, $CHCl_2$·CHCl·OEt. It also absorbs hydrogen chloride with formation of the compound CH_2Cl·CHCl·OEt, which seems to be identical with Lieben's dichlorether. When boiled with nitric acid, monochlorovinyl ethyl ether yields acetic and mono-

chloracetic acids; with phosphoric chloride, it yields trichlorethyl ether and eventually chlorethane. It reduces ammoniacal silver nitrate with production of a mirror, and when exposed to the air it rapidly changes to a vitreous mass of the composition $(C_4H_7ClO)_3 + H_2O$.

Trichlorethyl ether, $CHCl_2{\cdot}CHCl{\cdot}OEt$, obtained by the action of chlorine on the preceding compound, is a liquid which fumes in the air and boils at about 157° with partial decomposition. With sodium ethoxide, it yields dichloracetal, and with concentrated aqueous potash it yields *dichlorovinyl ethyl ether*, $CCl_2 : CH{\cdot}OEt$, which boils at 145°, has a sweet and penetrating odour, is insoluble in water, but dissolves in alcohol and ether, reduces ammonio-silver nitrate with production of a mirror, and absorbs bromine energetically. With chlorine, it yields *tetrachlorethyl ether* which boils at 180—185°, has an odour recalling that of mint and terebenthene, and seems to be identical with the ether obtained by Henry by the action of phosphoric chloride on chloral alcoholate.

Trichlorovinyl ethyl ether, $CCl_2 : CCl{\cdot}OEt$, is obtained by the action of concentrated aqueous potash on the preceding compound. It boils at about 160° under normal pressure, is insoluble in water, but dissolves in ether and alcohol; sp. gr. at 19° = 1·3322. When freshly prepared, it has an odour resembling that of mint, but in contact with air it loses hydrochloric acid and becomes pungent. It absorbs bromine and chlorine, and with the latter yields pentachlorethyl ether, $CCl_3CCl_2{\cdot}OEt$.

The vinyl ethyl ethers when freshly prepared are colourless and mobile, do not fume in the air, and have a pleasant odour which becomes more aromatic as the proportion of chlorine increases. They distil without decomposition under atmospheric pressure, but alter slowly and become acrid if exposed to the air. With ammonio-silver nitrate they give no precipitate of silver chloride, but gradually reduce it, with production of a mirror. The chlorine-derivatives of ethyl ether fume in the air and have an irritating odour, which however becomes more aromatic as the proportion of chlorine increases; they cannot be distilled without partial decomposition. They give an immediate precipitate of silver chloride with ammonio-silver nitrate, and when boiled with it reduce the silver to the metallic state without as a rule forming a mirror. C. H. B.

Ethyl and Methyl Hypochlorite. By T. Sandmeyer (*Ber.*, **19**, 857—861; compare Abstr., 1885, 1045).—The following method of preparing ethyl hypochlorite was found to be convenient: a glass tube 40 cm. long and 3 cm. wide, is drawn out at the lower end, and a glass tap fused on; the upper end is also drawn out. The tube is fitted into a condenser-tube through which a quick stream of water is passed when in use; it is then three-quarters filled with a solution of 1 part of sodium hydroxide in 1 part of alcohol and 9 parts of water, and a regular stream of chlorine is passed in through the tap—the tube being inclined as much as possible to reduce the pressure. The passage of chlorine through the solution must be stopped before it ceases to be absorbed.

Methyl hypochlorite, MeOCl, is prepared in the apparatus described above from a solution of 4 parts of soda in 3 parts of methyl alcohol and 36 parts of water. After chlorine has been passed through for some time, methyl hypochlorite is evolved as a gas. When ignited, it explodes with extreme violence; it is equally explosive in the liquid state. It boils at 10—12° at a pressure of 726 mm. When dry methyl hypochlorite and dry sulphur dioxide (in excess) are passed simultaneously into a cooled flask, methyl chlorosulphonate is obtained; this is a clear liquid which boils without decomposition at 132—133° under 722 mm. pressure. It has a very powerful odour. It has previously been prepared by Behrend (this Journal, 1877, ii, 289), but not in the pure state.

Ethyl chlorosulphonate (compare Behrend, *loc. cit.*, and Claësson, Abstr., 1879, 775) was obtained by passing dry sulphur dioxide through ethyl hypochlorite, and has all the properties previously ascribed to it (*loc. cit.*). N. H. M.

Oxidation of Mannitol. By F. W. Dafert (*Ber.*, **19**, 911—913). Iwig and Hecht have recently shown (this vol., p. 525) that mannitol, on oxidation with potassium permanganate, yields carbonic, formic, oxalic, tartaric, and erythritic acids, the last of which may have been mistaken for glucose. On the other hand, the author has proved that the first product of oxidation of mannitol by platinum black and potassium permanganate is dextrose. The discrepancy of the results is to be traced to differences of conditions under which the reaction was studied in the two cases. V. H. V.

Inversion of Cane-sugar in Sparkling Wines. By J. Moritz (*Bied. Centr.*, 1886, 276—277).—It is well known that the flavour of sparkling wines becomes finer and more agreeable with age. The author thinks that the cane-sugar syrup, which under the name of liqueur is added to all such wines at the time of bottling, undergoes a process of inversion, invert sugar having a finer and more agreeable taste than cane-sugar.

He found in a two-year bottled wine, prepared as usual, 12·2 per cent. of invert sugar, but no cane-sugar. He enumerates several factors which retard or accelerate the inversion. Alcohol retards; the presence of a little yeast greatly facilitates the change, as does an elevation of temperature; the presence of a very slight amount of tartaric acid renders the process of inversion very rapid. J. F.

Carbohydrate from the Seed of Lupinus Luteus. By E. Steiger (*Ber.*, **19**, 827—830).—Baeyer (*Landw. Versuchs-Stat.*, **9**, 168, and **14**, 164) and Eichhorn (*Landw. Versuchs-Stat.*, **9**, 275) have described briefly a dextrine-like substance, which they found in the seed of *Lupinus luteus*. It is soluble in alcohol, dextrorotatory, and converted by mineral acids into a sugar which reduces alkaline copper solution. The author has now investigated this subject more fully.

The husked and ground seeds were extracted with 80 per cent. alcohol, the free organic acids precipitated with lead hydroxide, and the alcohol then distilled off. The residue was diluted with water,

treated with tannin as long as a precipitate was formed, and then, without filtration, the excess of tannin removed with lead acetate. The filtrate was freed from lead by means of hydrogen sulphide, exactly neutralised with soda, and evaporated to a small bulk. The addition of absolute or 95 per cent. alcohol then precipitated the carbohydrate as a yellowish substance. After further purification (in which phosphotungstic acid proved a very useful precipitant for the nitrogenous organic impurities present), this substance was obtained as a white, hygroscopic powder, soluble in water. In ether and absolute alcohol, it is insoluble, but dissolves in boiling aqueous alcohol in proportion to the percentage of water present. The analytical results gave the formula $C_6H_{10}O_5$, and a 10 per cent. solution gave $[\alpha]_D = +148{\cdot}7$. It is not changed by diastase, and is oxidised by strong nitric acid to mucic acid. With acetic anhydride, it yields a triacetoderivative, $C_6H_7O_5Ac_3$. When heated with dilute sulphuric or hydrochloric acid, it yields galactose and no glucose. This carbohydrate very closely resembles galactin (or adopting Scheibler's nomenclature galactan), obtained by Muntz from the seed of the lucerne (*Medicago sativa*). The author, therefore, proposes to call it *β-galactan*. It is undoubtedly a different substance from A. Mayer's lactosin (Abstr., 1884, 980). L. T. T.

Acetone Phosphorus Compounds. By A. Michaelis (*Ber.*, **19**, 1009—1012; compare Abstr., 1885, 747).—*Diacetonephenylphosphinic acid*, $COMe{\cdot}CHPr^{\beta}{\cdot}PPhO{\cdot}OH + H_2O$, is prepared by mixing 20 grams of phosphenyl chloride with 30 grams of pure acetone, gradually adding 35 grams of phosphoric anhydride to the well-cooled mixture, and finally treating the mass with water. It crystallises in long plates, melts at 86°, and is sparingly soluble in cold water and in ether, very readily in alcohol. The *silver salt*, $C_{12}H_{16}PO_3Ag$, forms a colourless, crystalline mass.

Diacetonetolylphosphinic acid, $C_6H_{12}(C_7H_7)PO_3$, prepared in a similar manner from paratolyl phosphochloride, crystallises in small, lustrous, anhydrous plates, melts at 102—103°, is readily soluble in alcohol and ether, and is more soluble in hot water than the phenyl-compound. The silver salt crystallises in slender, lustrous needles.

A. J. G.

Formaldehyde and its Condensation. By O. Loew (*J. pr. Chem.* [2], **33**, 321—351).—Formaldehyde is conveniently prepared in the following way:—A current of dry air is drawn as quickly as possible through a half litre flask, half filled with methyl alcohol, then through a hard glass tube 30 cm. long, containing a cylinder of coarse copper gauze 5 cm. long, and then successively through an empty flask (300—400 c.c. capacity), and two flasks half filled with water. That part of the tube containing the copper gauze is surrounded with brass gauze and gently heated. When the alcohol vapour reaches the copper, the latter glows more or less, according to the rate of the current of air passing over it. The operation requires no attention beyond keeping up the supply of alcohol, and may be left night and day. A 15—20 per cent. solution of aldehyde was obtained in this way.

In like manner, ethers, hydrocarbons, and even bases can be converted into aldehydes.

Formose, $C_6H_{12}O_6$, is obtained by shaking a 3·5 to 4 per cent. solution of formaldehyde with an excess of milk of lime; after half an hour, the liquid is filtered, and nearly or quite saturated with lime. In 5 to 6 days, the odour of formaldehyde disappears, and a drop of the liquid shows a very great reducing power with Fehling's solution. The whole is then neutralised with oxalic acid, the filtrate evaporated to a syrup, mixed with an equal volume of strong alcohol and warmed for some hours, when the greater part of the calcium formate separates. The filtrate is evaporated at a moderate temperature to a thick syrup, dissolved in alcohol and treated with ether, which precipitates the sugar as a tenacious mass. The crude product was purified by partial precipitation. When dried at 90°, it forms a gum-like mass, and could not be obtained in the crystalline form. It has an intensely sweet taste, like that of cane-sugar syrup, which it generally resembles in its behaviour, as for instance towards phenylhydrazine. It is sparingly soluble in alcohol, insoluble in ether. When heated at 119—120°, it gives up the elements of water, and yields a compound of the formula $C_6H_{10}O_5$, having an intensely bitter taste. Formose gradually loses its reducing power for Fehling's solution, when digested with a 2 per cent. solution of sulphuric acid; warm strong hydrochloric acid decomposes it with formation of humous substances. It is more readily decomposed by alkalis than dextrose. It reduces an alkaline solution of potassium ferricyanide to ferrocyanide, and precipitates metals, such as gold, palladium, &c., from solutions of their salts. Like dextrose and levulose, it gives a red coloration when warmed with an alkaline picric acid solution; it also decolorises a solution of sodium sulphindigotate in presence of sodium carbonate. Other colour reactions are described. Formose is quickly acted on by bromine, yielding oxalic and trihydroxybutyric acids. The action of nitric acid and of nascent hydrogen was also tried, but without any very definite results.

Yeast was found to have no action on formose carefully freed from formic acid. When a 5 per cent. solution is kept for three weeks with 5 c.c. of hay water, 1 per cent. of peptone, precipitated calcium carbonate, and 0·1 per cent. of hydrogen dipotassium phosphate at the ordinary temperature, a small quantity of lactic and less succinic acid are formed. Mould spores act on formose with separation of a substance, which rotated polarised light 5° to the right.

Compounds of formose with *baryta*, *sodium chloride*, *&c.*, were prepared. The *phenyldrazine-compound*, $C_{18}H_{22}N_4O_3$, formed by the union of phenylhydrazine (2 mols.) and formose (1 mol.) with elimination of 3 mols. OH_2, is described. Formose resembles the glucoses and differs essentially from Carius' phenose (*Annalen*, **136**, 324), which is possibly an aromatic compound.

The substance obtained by Butlerow by the addition of lime-water to a boiling solution of "trihydroxymethylene," and described by him as methylenitan with the provisional formula $C_7H_{14}O_6$, is also formed by the action of lime at 70—90° on formose; it is a mixture con-

sisting chiefly of the saccharin of formose, $C_6H_{10}O_5$, already prepared and described by Tollens (Abstr., 1884, 293).

The condensation of formaldehyde to a sugar nearly related to the glucoses affords fresh evidence in support of v. Baeyer's theory of assimilation in plants. Attempts have been made to show that formaldehyde is an intermediate product between carbonic anhydride and dextrose, but without any definite results (compare Abstr., 1882, 243). The author, therefore, intends to investigate the external effect of formaldehyde on plants, and to ascertain whether starch is produced. The paper concludes with further remarks on the relation of formaldehyde to vegetable physiology. N. H. M.

Oxidation of Fatty Acids. By H. Carette (*Compt. rend.*, **102**, 692—693).—When stearic and palmitic acids are oxidised by prolonged boiling with a large excess of nitric acid of sp. gr. 1·36, succinic acid and normal propylenedicarboxylic acid are obtained in considerable quantity. Oleic acid also yields normal propylenedicarboxylic acid when oxidised in the same way (compare this vol., p. 335).

Normal propylenedicarboxylic acid is possibly identical with the lipic acid of earlier chemists. C. H. B.

Derivatives of Carbonic Anhydride. By T. Sandmeyer (*Ber.*, **19**, 862—867).—*Ethyl chlorimidocarbonate*, $NCl:C(OEt)_2$, is prepared by passing chlorine through the mixed solutions of 80 grams of caustic soda in 200 grams of alcohol, and 80 grams of 96—98 per cent. potassium cyanide in 600 c.c. of water, until the solution just ceases to turn red litmus-paper blue. Water is added, and the crystals which are then formed are washed with water and crystallised from ether. It forms large, colourless prisms, readily soluble in alcohol and ether, insoluble in water. It has a peculiar odour and melts at 39°. Hydrogen sulphide acts on it in presence of water with formation of ethyl carbonate, ammonium chloride, and sulphur. Dilute sulphuric acid decomposes it into ethyl carbonate, ammonium sulphate, and nitrogen chloride. Boiling aqueous potash solution has no action on it.

Methyl chlorimidocarbamate, $NCl:C(OMe)_2$, is prepared like the above compound; it melts at 20°. In its behaviour, it resembles the ethyl salt.

Ethyl imidocarbonate, $NH:C(OEt)_2$, is obtained by adding 15 grams of ethyl chlorimidocarbonate to a cooled solution of 11 grams of arsenic trioxide and 30 grams of potash in 120 grams of water. The whole is well shaken, care being taken that the temperature does not rise above 30°. The oil is separated and kept in contact with solid potash for 24 hours; it is then pure. It has an odour resembling that of trimethylamine, and mixes in all proportions with water. It does not distil without decomposition. When heated, it decomposes violently into ethyl chloride and urethane. Boiling aqueous ammonia converts it readily into guanidine. When heated with zinc-dust, it gives off the odour of carbylamine. Aniline hydrochloride acts on

it with formation of a *compound*, probably $NPh:C(OEt)_2$. Hydroxylamine hydrochloride also reacts with ethyl imidocarbonate, the chief product being *ethyl oximidocarbonate*.

Methyl imidocarbonate, $NH:C(OMe)_2$, is obtained in a manner similar to the ethyl salt, except that being soluble in water, it has to be extracted with ether. It has a strongly ammoniacal odour. The author thinks that the production of ethyl carbonate, carbaminate and chloride and ammonium chloride noticed by Würtz (*Annalen*, **79**, 286), when a solution of cyanic chloride in dilute alcohol is kept for some days, is due to the decomposition of ethyl imidocarbonate, formed by the union of cyanic chloride with 2 mols. of alcohol.

N. H. M.

Decomposition of Optically Inactive Compounds. By E. Bichat (*Compt. rend.*, **102**, 766—767).—A reply to Wyrouboff. (See this vol., pp. 445 and 446.)

Crystalline Forms of Potassium and Ammonium Hydrogen Tartrates. By A. Scacchi (*Zeit. Kryst. Min.*, **11**, 405—407).—Potassium hydrogen dextro- or lævo-tartrates: rhombic; $a:b:c = 1:0{\cdot}7168:0{\cdot}7373$. Potassium hydrogen racemate: monoclinic; $a:b:c = 1:0{\cdot}6156:0{\cdot}6455$. Ammonium hydrogen dextro- or lævo-tartrates: rhombic; $a:b:c = 1:0{\cdot}6946:0{\cdot}7085$. Ammonium hydrogen racemate: monoclinic; $a:b:c = 1:0{\cdot}6156:0{\cdot}6267$. Wyrouboff described these racemates as triclinic, giving for the potassium salt $a:b:c = 0{\cdot}7053:1:0{\cdot}7252$, and for the ammonium salt $a:b:c = 0{\cdot}7231:1:0{\cdot}7543$. The author has, however, failed to obtain them in any other than monoclinic forms.

A. J. G.

Colour-bases from Furfuraldehyde. By H. Schiff (*Ber.*, **19**, 847—849; compare Abstr., 1880, 391).—*β-Furfuronaphthyline*, $C_{10}H_7N:CH{\cdot}C_4H_3O$, is obtained by the direct union of furfuraldehyde and β-naphthylamine; a *hydrate* is first formed, and this gives up water yielding the above compound. It forms colourless, lustrous plates which melt at 85°. The *hydrochloride* crystallises in gold-coloured needles.

Secondary aromatic bases also yield chromogenic furfuraldehyde bases; *dimethylanilinefurfural hydrochloride*, $2C_6H_6MeN,C_5H_4O_2,HCl$, forms splendid violet crystals melting at 94°.

Tertiary aromatic bases react with furfuraldehyde only in presence of dehydrating agents.

Compounds were also obtained in which furfuraldehyde is united with two different aromatic bases; for instance, with aniline and methylaniline, with benzidine and aniline, &c. They form green to bronze-coloured compounds with a metallic lustre resembling that of magenta.

Aniline salts of aromatic amido-acids also react with furfuraldehyde to form similar compounds.

Ammonium furfuropicramate, $C_5H_4O_2,NH_2{\cdot}C_6H_2(NO_2)_2OH,NH_3$, is obtained by the action of furfuraldehyde on amidodinitrophenol in alcoholic solution. It forms lustrous, gold-coloured needles which, when heated to 185°, decompose without melting. It is decomposed by

the weakest acids into its constituents. Acetic anhydride decomposes it with formation of *acetyldinitramidophenol*, $NH_2{\cdot}C_6H_2(NO_2)_2{\cdot}OAc$. The latter forms small, nearly colourless prisms which melt at 193°.

N. H. M.

Physical Properties of Thiophen. By G. P. Grimaldi (*Gazzetta*, **16**, 63—64).—Schiff has recently found the values for the constants a, b, in the general isothermic equation $(p + \frac{a}{v^2})(v - b) = RT$, of Van der Waals (comp. Trans., 1884, 136) to be 0·0365 and 0·00496 respectively. But the author shows that by substituting these values for a and b, making $p = 1$, and T the absolute temperature of the experiment, the values obtained for R are not constant as the theory would indicate, but tend to decrease with increase of temperature. This result is in accordance with the conception of Clausius, that the internal pressure $\frac{a}{v^2}$ for constant volume should increase with the temperature.

V. H. V.

Thiophendisulphonic Acid. By H. Jaekel (*Ber.*, **19**, 1066—1067).—The copper salt, $C_4SH_2(SO_3)_2Cu + 4H_2O$, crystallises in needles; the silver salt, $C_4SH_2(SO_3Ag)_2$, crystallises in tufts or nodular aggregates of needles, and is moderately soluble in hot water.

A. J. G.

Constitution of Benzene. By A. Ladenburg (*Ber.*, **19**, 971—973).—It is here pointed out that the conversion of ethyl succinosuccinate into the ethyl salt of dihydroxyterephthalic acid, a reaction interpreted by Baeyer, is better explained by the author's prism formula than by Kekulé's formula for benzene.

V. H. V.

Xylene-derivatives. By A. Colson and H. Gautier (*Compt. rend.*, **102**, 689—692).—When ortho-xylene is heated in sealed tubes at 100° with a large excess of phosphorus pentachloride, it is converted with difficulty into *pentachloro-xylene*, $C_8H_5Cl_5$, a solid compound which melts at 53·6°, and is soluble in ether, alcohol, petroleum, and chloroform. When left in contact with dilute potash solution, it loses the whole of its chlorine, and is converted into an acid aldehyde. Paraxylene yields a mixture of the penta- and hexa-chloro-derivatives. The latter crystallises in transparent macled crystals which melt at 111°. Metaxylene also yields a hexachloro-derivative, which boils at about 286°, and is converted by the action of dilute alkalis into complex acid compounds containing chlorine. It follows that the pentachloride attacks the benzene nucleus in metaxylene, and in this respect metaxylene differs from its isomerides.

The tetrachloro-derivatives of the xylenes are easily saponified when boiled with water. Tetrachloroparaxylene yields terephthalic aldehyde melting at 113°. Tetrachlorortho-xylene yields an oily liquid if the crude product of hydrolysis is evaporated even under reduced pressure, but if the solution is exactly neutralised phthalic aldehyde is obtained as a pale yellow, crystalline solid which melts at about 52°. Tetrachlorometaxylene (b. p. 273°, sp. gr. 1·536)

yields an oil which gives with ammonia a reaction similar to that given by terephthalic aldehyde, that is, the solution becomes green, and a brownish-black precipitate is formed.

When pentachloro-xylene, $CHCl_2 \cdot C_6H_4 \cdot CCl_3$(1 : 2), is saponified with water, it yields orthophenyleneglyoxylic acid, $COH \cdot C_6H_4 \cdot COOH$, a lemon-yellow, crystallisable substance which melts at 97·2°; sp. gr. 1·404. This compound occupies the same position in the benzene series that glyoxylic acid does in the paraffin series. C. H. B.

Action of Phosphorus Pentachloride on Salts of Organic Acids. By A. Michael (*Ber.*, **19**, 845—847).—*Trichlorophenoxyethylene*, $CCl_2 : CCl \cdot OPh$, is obtained by slightly warming a mixture of equivalent weights of phenyl acetate and phosphorus pentachloride in a reflux apparatus until the evolution of hydrogen chloride ceases. The product is poured into water and distilled with steam; the oil thus obtained is boiled with alkali and again steam distilled. It melts at 25·5°. It is analogous to Geuther's trichlorethoxyethylene (*J. pr. Chem.* [2], **7**, 105), and can be obtained in a similar manner to that compound by the action of potassium phenoxide on perchlorethylene. A compound probably identical with that obtained by Geuther (*loc. cit.*) was prepared from ethyl acetate.

Metaphenyleneoxytrichlorethylene, $C_6H_4(O \cdot CCl : CCl_2)_2$, was prepared by the action of phosphorus pentachloride on metaphenylene acetate; it forms prisms melting at 53—54°. In like manner, the *compound* $C_6H_4<^{O}_{O}>CCl \cdot CCl_2H$ was obtained from the quinol-derivative. Compounds were also obtained from orcinol- and pyrogallol-derivatives. Phenyl propionate yielded the compound $C_2H_3Cl : CClOPh$, boiling at 114—118° (in a vacuum). Phenyl succinate reacts analogously. N. H. M.

Chlorocresols and Toluquinones. By A. Claus and H. Schweitzer (*Ber.*, **19**, 927—932).—*Dichlororthocresol*, purified from traces of the para-compound, crystallises in colourless needles, melting at 54°, sparingly soluble in cold, more soluble in hot water. On oxidation with chromic mixture, it yields di- and tri-chlorotoluquinone; the presence of the former has been overlooked in previous experiments. When reduced, the trichloro-derivative yields the corresponding quinol, melting at 212°, and distilling in vapour of water, whilst the dichloroquinol is not volatile under these conditions, and forms minute, colourless needles which melt at 120°.

If, however, the chromic oxidation process be conducted in dilute solution, avoiding excess of sulphuric acid and prolonged heating, the product formed is a monochlorotoluquinone, which crystallises in golden needles, melting at 90°, and is insoluble in cold water, more soluble in hot water, alcohol and chloroform. When reduced, it yields a quinol, crystallising in colourless needles, which melt at 115° and are volatile in vapour of water. As the dichlororthocresol yields a monochloroquinone on oxidation, one chlorine atom must be in the 1 : 4 position to the hydroxyl-group; of the

three possible formulæ, the authors consider Cl : Me : OH : Cl = 1 : 3 : 4 : 6 to be the most probable.

Dichlorometacresol crystallises in colourless needles, melts at 46°, and is almost insoluble in cold water, soluble in alcohol and ether. In the readiness with which it forms a combination with ammonia, it is intermediate between its two isomerides. When oxidised with chromic acid in acetic acid solution, it yields a mixture of di- and tri-chlorotoluquinone, but if the oxidation be effected in aqueous solution the former only is produced; it crystallises in golden leaflets, which melt with partial sublimation at 103°; its corresponding quinol crystallises in needles, sparingly soluble in cold, more soluble in hot water, alcohol, ether, and chloroform. As the dichlorometacresol yields a dichloroquinone on oxidation, neither of the chlorine-atoms can be in the para-position to the hydroxyl-group. V. H. V.

Pseudocumenyl Alcohol. By E. Hjelt and M. Gadd (*Ber.*, **19**, 867—868).—*Pseudocumenyl alcohol*, $C_6H_3Me(OH)_2$ [= 4 : 1 : 3], is prepared by boiling pseudocumenyl bromide (m. p. 97·5°, obtained by the action of bromine on pseudocumene at 140°; compare this vol., p. 452) with a solution of sodium carbonate. It melts at 77·5°, and dissolves readily in water and alcohol, sparingly in ether. When oxidised with chromic mixture, it is converted into Jacobsen's β-xylidenic acid (Abstr., 1882, 187). N. H. M.

Tribenzylamine-derivatives. By A. Marquardt (*Ber.*, **19**, 1027—1031).—*Tribenzylmethylammonium iodide*, $NMe(C_7H_7)_3I$, obtained by heating tribenzylamine and methyl iodide in sealed tubes on the water-bath, crystallises in white needles, melts at 184°, and is sparingly soluble in cold water, moderately soluble in alcohol. When treated with moist silver oxide, it yields the *hydroxide* $NMe(C_7H_7)_3{\cdot}OH$, a crystalline mass of strongly alkaline reaction; this when heated is resolved into methyl alcohol and tribenzylamine. The *platinochloride*, $(C_{22}H_{24}N)_2,PtCl_6$, melts at 197°. When tribenzylamine is heated with methyl iodide for some time at 150°, benzyl iodide and tetramethylammonium iodide are formed.

Tribenzylethylammonium iodide, $NEt(C_7H_7)_3I$, forms colourless, rhombic crystals, melts at 190°, and is moderately soluble in alcohol and hot water. The *isopropyl* compound, $NPr^{\beta}(C_7H_7)_3I$, crystallises in needles, melts at 170°, and is sparingly soluble in hot water. By the action of normal propyl iodide on tribenzylamine, either benzyltripropylammonium iodide or tetrapropylammonium iodide is formed according to the temperature.

A tetrabenzylammonium chloride could not be obtained by the action of benzyl chloride on tribenzylamine; hydrogen chloride was evolved, and a resinous product containing dibenzylamine and tribenzylamine hydrochlorides formed.

By the nitration of tribenzylamine, a *trinitrobenzylamine* was obtained; it forms colourless crystals, melts at 159°, is insoluble in water and alcohol, and is probably identical with that described by Strakosch (this Journal, 1874, 78). The main product of the reaction,

however, is a resinous nitro-compound readily soluble in alcohol; it could not be obtained in a state fit for examination. A. J. G.

Action of Sodium on Tribenzylamine. By C. L. Jackson and J. F. Wing (*Ber.*, **19**, 900—902).—When sodium is heated with twice its weight of tribenzylamine, at 150—160°, it acquires an intense purple colour which increases until the temperature of 190—200° is reached. The products of the reaction are benzene, toluene, sodium cyanide, lophine, a blue base, and a brown substance formed apparently by the reduction of the base. N. H. M.

Derivatives of Trichloroparamidophenol. By F. Lampert (*J. pr. Chem.* [2], **33**, 371—393).—In the preparation of trichloroparamidophenol by Schmitt and Andresen's method (Abstr., 1882, 611), small quantities of tri- and tetra-chloroquinol are formed. The identity of trichloroparamidophenol with the trichloramidophenol described by Hirsch (Abstr., 1881, 163), is shown by the fact that they both yield the same trichlorophenol (m. p. 53—54°, b. p. 252—253°).

Trichlorophenetoïl, $C_6H_2Cl_3{\cdot}OEt$, is obtained by the action of ethyl iodide on the sodium salt of trichlorophenol melting at 54°. It boils at 245—246° (uncorr).

Acetyltrichlorophenol, $C_6H_2Cl_3O{\cdot}OAc$, is prepared by boiling trichlorophenol with acetic chloride for two hours. It is a colourless oil boiling at 258—259° (uncorr.).

Trichloronitrophenol, $OH{\cdot}C_6HCl_3{\cdot}NO_2$, is formed when trichlorophenol is warmed with strong nitric acid. It crystallises in white needles melting at 146°, with evolution of reddish-brown vapour. The *sodium salt* forms gold-coloured needles. Trichloronitrophenol is also formed by the action of fuming nitric acid on trichlorophenol, but is converted into trichloroquinone by prolonged heating with the fuming acid. It yields trichloroparamidophenol when reduced. The constitution of trichloronitrophenol is therefore [OH : Cl_3 : NO_2 = 1 : 2 : 3 : 6 : 4 or 1 : 2 : 3 : 5 : 4].

Trichloronitrophenetoïl, $NO_2{\cdot}C_6HCl_3{\cdot}OEt$, is prepared in a manner similar to trichlorophenetoïl, and forms long, white needles melting at 68—69°; it resembles nitrophenol in its solubility.

When 1 : 2 : 4 : 6-trichlorophenoïl, melting at 68°, is heated for 36 hours at 210—220° with phosphorus pentachloride, it is converted into unsymmetrical tetrachlorobenzene; this reaction supports the constitution given above (compare Chandelon, Abstr., 1883, 1108). Trichlorophenol, melting at 54°, reacts with phosphorus pentachloride with formation of pentachlorobenzene melting at 85—86°. When the reaction is allowed to take place at the ordinary temperature with an excess of phosphorus pentachloride, and the product allowed to remain for 14 days, *phenyl trichlorophosphate* is formed. The latter melts at 173°, and is soluble in benzene.

These results point to the following constitutional formulæ for trichlorophenol melting at 53—54°:

[OH : Cl_3 = 1 : 2 : 3 : 5 or 1 : 2 : 3 : 6].

Trichlorodiazophenolsulphonic acid, $OH\cdot C_6HCl_3\cdot N_2\cdot SO_3H$, is obtained by adding trichlorodiazophenol (Hirsch, *loc. cit.*) to a concentrated aqueous solution of sodium sulphite. It is a yellow, crystalline substance; when heated above 200°, it decomposes with explosive violence. The *sodium* and *barium* salts were prepared; the latter forms reddish-yellow crystals which explode when heated.

Trichloriodophenol, $C_6HCl_3I\cdot OH$, is prepared by the action of hydriodic acid on trichlorodiazophenol; the reaction is very violent. The product has to be boiled repeatedly with sulphurous acid and with animal charcoal to decolorise it, and is then recrystallised from very dilute alcohol cooled below 0°. It forms white needles melting at 79—80°, and dissolves readily in alcohol.

Trichloriodophenetoïl, $C_6HCl_3I\cdot OEt$, forms yellow needles melting at 60—61°. It is more sparingly soluble in alcohol than trichloriodophenol. Chlorine converts it, with evolution of iodine-vapour, into perchlorophenol melting at 186—187°. N. H. M.

Imidochlorides and their Reactions. By F. Just (*Ber.*, **19**, 979—988).—In this paper, a series of imidochlorides are described of the general formula RCCl : NR, obtained by the action of phosphoric chloride on the amines, and also their reactions with various compounds, especially sodium ethyl malonate.

Benzoyl-paratoluidimide chloride, $CPhCl : N\cdot C_6H_4Me$ [NCClPh : Me = 1 : 4], prepared by the action of phosphoric chloride on benzoylparatoluidine, forms large, prismatic crystals melting at 52°, and efflorescing on prolonged exposure. With paratoluidine, it yields benzenylditolylamimide, $C_7H_7\cdot N : CPh\cdot NH\cdot C_7H_7$. The corresponding ortho- and meta-derivatives from benzoylortho- and benzoylmeta-toluidine could not be obtained in a state fit for analysis.

Benzoyl-β-naphthylamimide chloride, $CPhCl : N\cdot C_{10}H_7$, prepared from benzoyl-β-naphthylamine and phosphoric chloride, crystallises in leaflets which melt at 68°; it is gradually converted into benzoyl-β-naphthylamine on exposure to air. The corresponding α-derivative, of similar crystalline appearance, melts at 60°.

These imidochlorides react with sodium ethyl malonate, forming two classes of derivatives, namely, those in which the imido-grouping replaces the sodium-atom, and, secondly, disubstitution-products derived probably by the intermediate formation of a monosubstituted sodium-derivative. Thus benzoyl-paratoluidimide chloride yields ethyl paratolylbenzylmalonate, $CH(COOEt)_2\cdot CPh : NC_6H_4Me$, a viscid oil; the corresponding ortho-derivative forms strongly refractive crystals belonging to the mono- or tri-clinic system.

Similarly *benzoyl-β-naphthylamimide chloride* yields ethyl β-naphthylbenzenylmalonate, $CH(COOEt)_2\cdot CPh : NC_{10}H_7$, a crystalline substance melting at 140·5°; the corresponding α-derivative melts at 145·5°.

The ethereal salts above described are analogous to the ethereal salts of anilbenzenylmalonates in so far that when heated with dilute hydrochloric acid in sealed tubes they are decomposed into a primary amine, benzophenone, ethyl chloride, and carbonic anhydride.

V. H. V.

Isonitroso-derivatives. By E. Beckmann (*Ber.*, **19**, 988—993).—When diphenylacetoxime is heated with phosphoric chloride, it yields a monochloro-derivative which crystallises in rhombic tables, melting at 41°, and emitting a disagreeable odour. It is slowly decomposed by water, forming, not the original diphenylacetoxime, but a compound isomeric with it. The explanation of these reactions is to be found in an interchange of the chlorine-atom and phenyl-group during the replacement of the hydroxyl by chlorine, thus: (i) $CPh_2 : NOH + PCl_5 = CPh_2 : NCl + PCl_3O + HCl$; and (ii) $CPh_2 : NCl = CPhCl : NPh$, or benzophenonechlorimide, as intermediate product, is converted into benzanilidimide chloride. The latter, as shown by Wallach, is transformed by water into benzanilide, $CPhCl : NPh + OH_2 = Ph{\cdot}CONPh + HCl$, the reverse change to which can be effected by phosphoric chloride.

By this series of reactions, therefore, a ketone is converted into the amide derived from a primary amine; and by an analogous reaction the aldehyde should be converted into an amide, as benzaldehyde into benzamide. At present, the author is examining the question as to the general nature of these transformations. V. H. V.

Triphenylarsine. By B. Philips (*Ber.*, **19**, 1031—1035).—Triphenylarsine hydroxide is most conveniently prepared by treating triphenylarsine bromide with soda. Hydrogen sulphide converts it into the sulphide, nascent hydrogen reduces it to triphenylarsine.

Triphenylarsine hydroxynitrate, $OH{\cdot}AsPh_3{\cdot}NO_3$, obtained by the action of nitric acid on the hydroxide, crystallises in long, lustrous needles, and melts at 84°.

Trinitrotriphenylarsine oxide, $AsO(C_6H_4{\cdot}NO_2)_3$, formed by the nitration of the hydroxide, is a crystalline, colourless substance; it melts at 254°, explodes on further heating, is insoluble in alcohol and ether, and readily soluble in glacial acetic acid; an intensely red, isomeric substance soluble in boiling alcohol is formed at the same time.

Triamidotriphenylarsine, $As(C_6H_4{\cdot}NH_2)_3$, is formed by the reduction of trinitrotriphenylarsine oxide; it is a colourless, crystalline substance, melts at 176°, and is insoluble in water, readily soluble in alcohol and dilute acids. The *hydrochloride*, $As(C_6H_4{\cdot}NH_2,HCl)_3$, forms a pale-red, crystalline mass; the platinochloride was also prepared. The *acetyl*-derivative, $As(C_6H_4{\cdot}NHAc)_3$, melts at 230°. A bromo-derivative is obtained as a white, pulverulent precipitate on adding bromine-water to a solution of the hydrochloride.

A. J. G.

Aromatic Silicon Compounds. By A. Polis (*Ber.*, **19**, 1012—1024; compare Abstr., 1885, 973).—Tetraphenylsilicon melts at 233°, not at 228° as previously stated (*loc. cit.*); it boils without decomposition at a temperature above 530°. It crystallises in the tetragonal system; $a : c = 1 : 0{\cdot}043969$, and has a sp. gr. 1·078 at 20°. By the action of bromine, it is converted into bromobenzene and complex phenyl-silicon compounds. Of these, the only one isolated had the formula $C_{18}Si_4H_{16}O_7$ = *trisilicobenzoylsilicic acid*, $OH{\cdot}Si(O{\cdot}SiPhO)_3$? This must owe its formation to the presence of moisture; it forms a white powder, is readily soluble in ether and chloroform, very

sparingly in alcohol, insoluble in light petroleum and acetic acid, and readily soluble with decomposition in alkalis.

Tetranitrotetraphenylsilicon, $Si(C_6H_4{\cdot}NO_2)_4$, is obtained by cautiously adding tetraphenylsilicon to a mixture of nitric and sulphuric acids immersed in a freezing mixture. It forms a pale-yellow powder, melts between 93° and 105°, and explodes at higher temperatures; it is readily soluble in benzene, chloroform, and hot acetic acid, nearly insoluble in alcohol and light petroleum. It is not improbable that it is a mixture of two isomerides.

Triphenylsilicon chloride, $SiPh_3Cl$, is obtained by heating tetraphenylsilicon (1 mol.) with phosphoric chloride (1 mol.) for 1½ hours at 180°. It forms small, colourless crystals, fumes on exposure to air, melts at 88—90°, can only be distilled unaltered under reduced pressure, and is readily soluble in light petroleum, ether, benzene, chloroform, and carbon bisulphide. Water converts it into the silicon alcohol, and in alcohol it dissolves with formation of the corresponding ethyl ether.

Triphenylsilicol, $SiPh_3{\cdot}OH$, is obtained by boiling the chloride with water, best with addition of ammonia; it forms colourless, transparent crystals, melts at 139—141°, can be distilled unchanged, and is readily soluble in ether, alcohol, chloroform, and benzene.

Diphenylsilicon dichloride, $SiPh_2Cl_2$, obtained by heating tetraphenylsilicon (1 mol.) with phosphoric chloride (2 mols.), is a colourless liquid boiling at 230—237° under 90 mm. pressure.

Tetraparatolylsilicon (*loc. cit.*) crystallises in the monosymmetric system, $a : b : c = 1{\cdot}12616 : 1 : 0{\cdot}94196$; $\beta = 71° 9{\cdot}5'$; it has a sp. gr. = 1·0793 at 20°, and boils above 450°. When treated with nitric acid, it is decomposed with formation of silica and paradinitrotoluene.

Tetrametatolylsilicon, $Si(C_7H_7)_4$, is obtained by the action of sodium on a mixture of silicon chloride and metabromotoluene. It crystallises in long, pale-yellow prisms, probably of the monosymmetric system, melts at 150·8°, boils without decomposition at above 550°, has a sp. gr. = 1·1188 at 20°, is readily soluble in benzene and chloroform, more sparingly in carbon bisulphide, ether, acetic acid, and light petroleum, and is insoluble in alcohol.

Tetrabenzylsilicon (*loc. cit.*) crystallises in monosymmetric prisms, and has a sp. gr. = 1·0776 at 20°. A. J. G.

Crystallographical Notices. By C. Soret (*Zeit. Kryst. Min.*, **11**, 431—434).—Ammonium metaxylene-phthaloylate,

$$C_6H_3Me_2{\cdot}CO{\cdot}C_6H_4{\cdot}COONH_4:$$

asymmetric; $a : b : c = 0{\cdot}5173 : 1 : ?$ $\alpha = 99° 11'$, $\beta = 94° 53'$, $\gamma = 90° 5'$. Pseudocumenephthaloylic acid: monosymmetric; $a : b : c = 1{\cdot}0013 : 1 : 1{\cdot}1181$, $\beta = 71° 32'$. Methyl diacetotartrate: monosymmetric; $a : b : c = 1{\cdot}0521 : 1 : 1{\cdot}0065$, $\beta = 87° 54'$. Ethyl diacetotartrate: monosymmetric; $a : b : c = 0{\cdot}7480 : 1 : 0{\cdot}9541$, $\beta = 88° 11'$.

Basic derivative of furfurobutylene, $N\langle^{C{\cdot}C_4H_3O}_{CMe_2}$: monosymmetric; $a : b : c = 1{\cdot}3804 : 1 : 1{\cdot}1273$, $\beta = 48° 25'$. Diphthalyl bromide:

monosymmetric; $a : b : c = 0{\cdot}5781 : 1 : 1{\cdot}4531$, $\beta = 82° 29'$. Methyl tetrachlorophthalate: rhombic; $a : b : c = 0{\cdot}5325 : 1 : 0{\cdot}4688$. Perchlorophthalic anhydride, C_8Cl_6O: asymmetric; observed faces 0P, ∞'P, ∞P'. A. J. G.

Action of Nitrous and Hyponitric Acids on some Unsaturated Compounds. By S. Gabriel (*Ber.* **19**, 836—842).—The author has already described (Abstr., 1885, 902 and 1229) the action of nitrous and hyponitric acids on benzylidenephthalide and similar compounds. He has now further extended these investigations.

Ethinediphthalide (formerly described as ethinediphthalyl, Abstr., 1880, 230; and Roser, Abstr., 1885, 165), was suspended in glacial acetic acid, which was then saturated with nitrous acid and heated whilst the current of gas was still passing. The yellow crystals were gradually converted into white needles of dinitroethinediphthalide, $CO<_{-O-}^{C_6H_4}>C(NO_2)\cdot CH(NO_2)\cdot CH : C<_{-O-}^{C_6H_4}>CO$. This substance becomes yellow at 140°, and melts with decomposition at 160°. It is only sparingly soluble in the usual solvents. When boiled with glacial acetic acid, it gives off nitrous fumes, and is gradually converted into *nitroethinediphthalide*, $C_{18}H_9O_4(NO_2)$, which crystallises out in yellow needles, easily soluble in nitrobenzene, sparingly so in the usual solvents, and melts at 240° with decomposition. The same compound may be obtained by the addition of an equal volume of alcohol to the glacial acetic acid filtrate from the original crystals of the dinitro-derivative.

In the preparation of ethinediphthalide, the mixture of succinic acid, phthalic anhydride, and sodium acetate is heated at 210—220°; but if the temperature is allowed to rise to 250—260° ethylidenephthalide (phthalethylidene), already described by Roser (this vol., p. 243), is obtained. The author finds the melting point to be 63—64°, whilst Roser gives 67—69°. This compound, when treated with nitrous acid as above, gives a hard, amorphous substance still under investigation. If, however, the nitrous is replaced by hyponitric acid, *dinitroethylidenephthalide*, $CO<_{-O-}^{C_6H_4}>C(NO_2)\cdot CH(NO_2)\cdot CH_3$, is formed; this crystallises in transparent prisms melting at 90°, and soluble in boiling alcohol. With alcoholic ammonia, ethylidenephthalide yields *propiophenoneorthocarboxylamide*, $EtCO\cdot C_6H_4\cdot CONH_2$. This amide crystallises in needles, easily soluble in alcohol and ether, sparingly so in benzene and chloroform. It melts at 159°.

The author has also studied the action of ammonia on ethylenedibenzoylorthocarboxylic acid, $C_2H_4(CO\cdot C_6H_4\cdot COOH)_2$, in the hopes of obtaining compounds analogous in constitution to benzalphthalimidine, but the reaction does not appear to take place in that direction. A substance of the formula $C_{18}H_{13}NO_4$ was obtained, which proved to be a bibasic acid. It crystallises in needles, which melt at 230—232°, and are soluble in boiling alcohol. With nitrous acid, it yields a compound of the formula $C_{18}H_{10}N_2O_5$, which crystallises in small, rhombic plates, melts at 210°, dissolves sparingly in boiling alcohol, and gives the

nitroso-reaction with phenol and sulphuric acid. These substances are still under investigation, but the author suggests

$$COOH\cdot C_6H_4\cdot C<\begin{matrix}CH\cdot CH\\ -NH-\end{matrix}>C\cdot C_6H_4\cdot COOH$$

as the probable constitution of the compound $C_{18}H_{13}NO_4$.

L. T. T.

Phthalylaspartic Acid. By A. Piutti (*Gazzetta*, **16**, 1—29).—*Phthalylaspartic acid*, $COOH\cdot CH_2\cdot CH(COOH)\cdot NC_2O_2 : C_6H_4$, is prepared by melting phthalic anhydride with aspartic acid or asparagine hydrochloride, the molecules of the two compounds coalescing with elimination of the elements of a molecule of water. It crystallises in small prisms, which melt at 225°; it is soluble in alcohol, insoluble in ether, and soluble in cold concentrated sulphuric acid, but is reprecipitated on dilution. Its ethyl salt is a heavy oil, soluble in alcohol; it is converted by a current of ammonia-gas into ammonium phthalimide, $C_6H_4C_2O_2N(NH_4)$, a crystalline precipitate, decomposed at 219° into its constituents. With aniline, the acid is converted into the phenylimide, $C_6H_4 : C_2O_2 : N\cdot CH\begin{matrix}\\ |\\ CH_2\end{matrix}\!\!>C_2O_2 : NPh$, which crystallises in prismatic needles melting at 263°, moderately soluble in alcohol, ether, and benzene. With diphenylamine, the acid yields *diphenylphthalylasparagine*, $CONPh_2\cdot C_2H_3(COOH)\cdot NC_2O_2 : C_6H_4$, of which there are three modifications: one crystallising in long silky needles containing $2H_2O$ and melting at 112°, the second in prisms or rhombic tables containing $1H_2O$ and melting at 193°, and the third in highly refractive crystals, anhydrous, and melting at 203—202°. With ammonia, the first modification yields *diphenylasparagine*, melting at 230°, and phthalamide, the second an ammonium salt, not further investigated, and the third a similar ammonium salt decomposed on prolonged heating at 180° in sealed tubes, yielding a corresponding *diphenylasparagine*, melting at 160° with decomposition.

In like manner, by heating these modifications with alcoholic ammonia two isomeric *phthalyldiphenylaminaspartides* are obtained, melting respectively at 273° and 286°; when heated with excess of alcoholic ammonia in sealed tubes, these are converted into a *diphenylamine-fumaride*, $C(NPh_2)_2<\begin{matrix}CH : CH\\ -O-\end{matrix}>CO$, crystallising in glistening needles which melt at 275°.

Phthalylmethylphenylasparagine, from phthalylaspartic acid and methylaniline, yields an *aspartide*, crystallising in needles which melt at 260° with decomposition; from this a *methylphenylfumaride* was obtained, crystallising in tufts of needles which melt at 187·5°; it is soluble in ether, and yields a dibromo-derivative, soluble in ether and alcohol, and melting at 206° with decomposition. V. H. V.

Tartramido- and Malamido-benzoic Acids. By H. Schiff (*Annalen*, **232**, 156—168).—By heating a mixture of tartaric and metamidobenzoic acids at 150—160° for some hours, a mixture of tartaryl-mono- and di-benzamic acids and their anhydrides is

obtained, and can be separated by treatment with water, in which the mono-compounds only are soluble.

Tartaryldibenzamic acid, $C_2H_2(OH)_2(CO\cdot NH\cdot C_6H_4\cdot COOH)_2$, is separated from its anhydride by solution in boiling alcohol; it is a nearly colourless, micro-crystalline powder. It dissolves readily in alkalis, yielding yellow salts; the copper salt, $C_{18}H_{14}N_2O_8(CuOH)_2$, forms bluish, crystalline flocks. Both the acid and its anhydride are converted into tartrate and amidobenzoate when boiled with alkalis. The inner anhydride, *tartrandibenzamic acid*,

$$CO\begin{<}CH\cdot CH(OH)\cdot CO\cdot NH\cdot C_6H_4\cdot COOH \\ N\cdot C_6H_4\cdot COOH\end{<}\ ,$$

is obtained as above mentioned, and is also formed by heating the acid at 180—200°, or by boiling it with acetic anhydride; it forms a greenish-yellow powder, decomposes at 300°, and is insoluble in water and alcohol. A copper salt, $(C_{18}H_{11}N_2O_7)_2Cu_3$, is described.

Tartrylbenzamic acid, $COOH\cdot C_2H_2(OH)_2\cdot CO\cdot NH\cdot C_6H_4\cdot COOH$, crystallises in straw-yellow crusts or nodular aggregates, or when perfectly pure in colourless plates of fatty lustre. It decomposes carbonates, and forms readily soluble salts with the alkalis and alkaline earths. Its inner anhydride, *tartranbenzamic acid*, $CO\begin{<}CH\cdot CH(OH)\cdot COOH \\ N\cdot C_6H_4\cdot COOH\end{<}$, crystallises in yellow crusts or, when less pure, in plates, which fluoresce splendidly. It is readily converted into tartrylbenzamic acid when heated with water. Its barium and copper salts are described. *Tartranilbenzamic acid*, $COOH\cdot C_6H_4\cdot C_3H_3NO_2\cdot CO\cdot NHPh$, formed by heating tartranbenzamic acid in alcoholic solution with aniline, crystallises in colourless, silky needles, melts at 245—246° with decomposition, and yields an acetyl-derivative crystallising in colourless needles and melting at 197—200° with incipient decomposition. When tartrylbenzamic acid or its anhydro-acid is heated at 200—210°, a second anhydride, *benzamtartridic acid*, $C_{11}H_7NO_5$, seems to be formed.

Tartryldibenzamamidic acid,

$$CONH_2\cdot C_6H_4\cdot NH\cdot CO\cdot C_2H_2(OH)_2\cdot CO\cdot NH\cdot C_6H_4\cdot COOH,$$

is obtained by heating a mixture of tartrylbenzamic acid and amidobenzamide at 140°. It is a white powder, insoluble in water, sparingly soluble in boiling alcohol, readily soluble in alkalis. The copper salt, $C_{18}H_{15}N_3O_7Cu + H_2O$, is described. The corresponding *imide* seems to be formed at the same time, and is obtained in larger quantity by heating the amido-acid for some hours at 150—160°; it crystallises in small plates.

Malyldibenzamic acid, $OH\cdot C_2H_3(CO\cdot NH\cdot C_6H_4\cdot COOH)_2$, is obtained by heating equimolecular proportions of malic and metamidobenzoic acids for some time at 140—150°. It forms a lustrous white, mealy powder, but little soluble in hot water or alcohol. The copper salt, $(C_{18}H_{13}N_2O_7)_2Cu_3$, forms a blue powder insoluble in water.

A. J. G.

Benzenetrisulphonic Acid. By C. L. Jackson and J. F. Wing (*Ber.*, **19**, 898—900).—Benzenetrisulphonic acid is conveniently prepared by heating 5 parts of potassium benzenemetadisulphonate in a dish with 6 parts of sulphuric acid. It is not advisable to take more than 35 grams of the potassium salt at a time. As soon as the effervescence caused by the separation of the water of crystallisation ceases, the acid begins to fume. When the fuming diminishes and the mass becomes pasty and begins to swell up, the reaction is finished. The reddish-brown product is dissolved in water, and converted first into a barium and then into a potassium salt.

The formation of benzenetrisulphonic acid, as described, is shown to be due to the presence of hydrogen potassium sulphate. The formation of toluenetrisulphonic acid by Claësson's method (Abstr., 1881, 429), namely, by heating potassium toluenedisulphonate with chlorosulphonic acid, is probably also due to the presence of hydrogen potassium sulphate. *Benzenetrisulphonic chloride* melts at 184°; the *amide* melts at 306°. When the potassium salt is heated with potassium cyanide, a nitrile is formed, which yields trimesic acid. The sulphonic acid has therefore the constitution [1 : 3 : 5].

N. H. M.

Direct Conversion of Aromatic Sulphonic Acids into the Corresponding Amido-compounds. By C. L. Jackson and J. F. Wing (*Ber.*, **19**, 902—903).—When a mixture of the theoretical quantities of sodamide, prepared by Beilstein and Geuther's method (*Annalen*, **108**, 88), with potassium benzenesulphonate is carefully heated (the heating being stopped before the formation of brown drops), and the product distilled with steam, aniline and diphenylamine are obtained. The formation of the latter compound is probably due to the presence of an excess of sodium in the amide. The yield of aniline was 10 per cent. of the theoretical amount, and could probably be raised with care.

Potassium benzenedisulphonate reacts with sodamide, and yields a product which gives several reactions characteristic of metadiphenylenediamine.

When tribromaniline dissolved in toluene is treated with sodamide, the solution acquires an intense purple colour. N. H. M.

Naphthalene-derivatives. By E. Lellmann and A. Remy (*Ber.*, **19**, 796—807).—The authors find that the nitracetonaphthalide melting at 171°, first described by Andreoni and Biedermann (*Ber.*, **6**, 342; see also Abstr., 1884, 751), is not a distinct compound, but a mixture of equal proportions of the ortho- and para-nitro-α-acetonaphthalides melting at 199° and 190° respectively. In the nitration of α-acetonaphthalide, these two compounds are alone produced, but the whole of the ortho-compound (which is only formed in small quantities) crystallises with an equal quantity of the para-derivative to form the apparently homogeneous substance melting constantly at 171°. The separation of the two isomerides was effected by adding to a hot alcoholic solution exactly enough aqueous potash to saponify half the substance taken. After about 24 hours, paranitro-

naphthylamine crystallised out, the orthonitronaphthalide, which was almost entirely unacted on, separating out on further standing.

Orthonitro-α-acetonaphthalide, $C_{10}H_6(NO_2)\cdot NHAc$ [$NHAc : NO_2 = 1 : 2$], thus obtained forms yellow needles sparingly soluble in alcohol, more easily in glacial acetic acid, and melting at 199°. When equal quantities of the pure ortho- and para-compounds in alcoholic solution were allowed to crystallise together, the characteristic needles, melting at 171°, were re-formed. That the substance melting at 199° was really an ortho-derivative was proved by subjecting it to the action of tin and hydrochloric acid, when *naphthylene-ethenylamidine* (ethenylnaphthalenediamine), $C_{10}H_6<\overset{NH_2}{\underset{N}{}}>C\cdot CH_3$, described by Prager (Abstr., 1885, 1239), was obtained as a white, non-crystalline substance yielding a *hydrochloride* which crystallises in soluble needles (see also Jacobsen, Abstr., 1882, 204). The *platinochloride*,

$$(C_{12}H_{10}N_2)_2,H_2PtCl_6,$$

forms yellow crystals; the *sulphate*, $C_{12}H_{10}N_2,H_2SO_4$, melts at 269°; the *picrate*, $C_{12}H_{10}N_2,C_6H_2(NO_2)_3\cdot OH$, forms golden-yellow needles melting at 242°. When saponified with the calculated quantity of potash, the orthonaphthalide yields orthonitro-α-naphthylamine (this vol., p. 471), and when heated with excess of potash, β-nitronaphthol. With acetic anhydride, the amine re-forms the aceto-derivative melting at 199°, and not, as previously stated, a compound melting at 194°. When boiled with a hydrochloric acid solution of stannous chloride, the nitronaphthylamine yields Griess' orthodiamidonaphthalene (Abstr., 1883, 183); this melts at 98·5°, not 95° as previously stated. It is a very feeble base, and yields a *hydrochloride*, $C_{10}H_6(NH_2)_2,2HCl$, which readily gives up hydrochloric acid, and a *sulphate*,

$$(C_{10}H_8N)_2,H_2SO_4,$$

crystallising in silvery scales. It is also undoubtedly identical with the diamine described by Lawson (Abstr., 1885, 802 and 1238), and with that obtained by Koreff (this vol., p. 363). The α-nitro-β-acetonaphthalide obtained by Jacobsen (Abstr., 1882, 204) forms rhombic crystals, $a : b : c = 0{\cdot}4317 : 1 : 0{\cdot}3971$. The base obtained by Ilinski by the reduction of orthonaphthyleneoxime-imide (this vol., p. 474) does not appear to be identical with the above base, as its hydrochloride contains only 1 mol. HCl, but is probably a di-imidonaphthalene, and not a diamine.

The compound previously described as δ-nitracetonaphthalide, melting at 143°, is really *paranitro-α-diacetonaphthalide*,

$$C_{10}H_6(NAc_2)\cdot NO_2 \quad [NAc_2 : NO_2 = 1 : 4];$$

when pure, it melts at 144°, and can be obtained by heating paranitronaphthylamine with excess of acetic anhydride. When boiled with alcoholic ammonia, one acetyl-group is eliminated, and paranitro-α-acetonaphthalide is formed. In like manner, the β-nitracetonaphthalide (m. p. 115°) described in the same communication proved to be *orthonitro-α-diacetonaphthalide*, $C_{10}H_6(NAc_2)\cdot NO_2$, and gave up one acetyl-group when boiled with ammonia L. T. T.

General Method for Determining the Constitution of Aromatic Diamines. By E. Lellmann (*Ber.*, **19**, 808—810).—As Lawson's inability to obtain a thiocyanate additive product with α-β-diamidonaphthalene (*Ber.*, **18**, 2425) seemed to point to the method proposed by the author (Abstr., 1885, 976) being inapplicable to diamines of the naphthalene series, the author has repeated Lawson's experiments. With allyl isothiocyanate, he readily obtained *naphthylene-diallylthiocarbamide*, $C_{10}H_6(NH{\cdot}CS{\cdot}NH{\cdot}C_3H_5)_2$. It crystallises in small, silky needles, which at 170° begin to decompose into diallylthiocarbamide and naphthylenethiocarbamide, $C_{10}H_6{:}(NH_2){:}CS$, a substance closely resembling the corresponding tolylene compound, and only melting at a very high temperature. Corresponding compounds were obtained with phenyl isothiocyanate. L. T. T.

Sandmeyer's Reaction. By E. Lellmann and A. Remy (*Ber.*, **19**, 810—811).—Applying this reaction (Abstr., 1884, 1311; and 1885, 149) to the naphthalene series, the authors have succeeded in isolating one of the intermediate products which Sandmeyer believed to be formed, but, from their extreme instability in the benzene series, was unable to isolate.

When a freshly-prepared solution (cooled with ice) of β-diazonaphthalene bromide is poured slowly into a solution of cuprous bromide in hydrobromic acid (sp. gr. 1·5), a red precipitate is formed of the formula $C_{10}H_7N_2Br,Cu_2Br_2$. If the operation is reversed by the cuprous bromide being added to the diazo-solution, a black precipitate is formed, which at once undergoes decomposition. On keeping, the red substance gradually blackens, β-bromonaphthalene being produced. This reaction takes place readily if the compound is boiled with water.

With cuprous chloride and β-diazonaphthalene chloride, a pale-yellow precipitate was obtained, but it was so unstable that no definite analyses could be obtained. L. T. T.

Isomeric Naphthyl Phenyl Ketones. By Rospendowski (*Compt. rend.*, **102**, 872—875).—The two isomeric naphthyl-phenyl ketones can be readily obtained by the action of aluminium chloride on a mixture of benzoic chloride and naphthalene, the β-derivative being formed in much larger proportion than when zinc is used as in Merz and Grucarevic's process. *α-Naphthyl phenyl ketone* forms colourless, transparent, crystalline granules, which have a brilliant lustre, and melt at 75·5°. *β-Naphthyl phenyl ketone* forms long, silky, white needles which melt at 82°. Both isomerides yield naphthalene and sodium benzoate when heated with soda-lime. The nitro-derivatives have not yet been obtained in a pure state. With bromine, α-naphthyl phenyl ketone yields a mono-bromo-derivative, crystallising in colourless, transparent, square tables, which melt at 100·5°, and distil without decomposition. When distilled with excess of soda-lime, this bromo-derivative yields benzene and β-naphthol, and is therefore a β-derivative.

Oxidation of the ketones with nitric acid or potassium perman-

ganate gives no satisfactory results, but repeated treatment of the α-derivative with chromic mixture yields *benzoylphthalic acid*, $CPhO{\cdot}C_6H_3(COOH)_2$ [1 : 2 : 3], which may be purified by recrystallising the lead salt. It forms white rhombohedral lamellæ, which can be recrystallised from ether in the form of colourless transparent tables melting at 155°. This acid decomposes carbonates with effervescence, and dissolves somewhat easily in warm water, but is not volatile in water vapour. It is very soluble in alcohol, ether, &c. Barium benzoylphthalate is somewhat soluble in water, and the silver salt is still more soluble. C. H. B.

Chlorophyll, and the Reduction of Carbonic Anhydride by Plants. By C. Timiriazeff (*Compt. rend.*, **102**, 686—689).—When a dilute alcohol solution of chlorophyll is subjected to the action of nascent hydrogen (from zinc and acetic acid), its colour changes to straw-yellow, whilst if the solution is strong it becomes reddish-brown by daylight and ruby by lamplight. This solution has a definite absorption-spectrum, which is characterised by the absence of band No. 1 in the red, and by the presence of a broad absorption-band, which occupies the position of band No. 2 and the spaces between bands 1 and 2 and bands 2 and 3. The solution oxidises readily when exposed to air, and becomes green, owing to the regeneration of the chlorophyll. The absorption of oxygen takes place very rapidly even in an atmosphere containing only a very small proportion of this gas, and is indicated by the almost instantaneous appearance of the band No. 1. The author gives to this product of reduction the provisional name *protochlorophyllin* or *protophyllin*.

If the yellow or red solution is enclosed in a tube containing carbonic anhydride, it rapidly becomes green when exposed to light, but if kept in the dark the solution retains its colour and characteristic absorption-spectrum for any length of time. If the tubes contain hydrogen instead of carbonic anhydride, no change takes place either on exposure to light or in the dark.

These results seem to indicate a reduction of carbonic anhydride by means of chlorophyll entirely out of contact with any vegetable organism, but further experiments are necessary before this point can be considered as definitely decided. C. H. B.

Constitution of Pyrroline. By G. Ciamician (*Gazzetta*, **16**, 46—63).—The author in this paper gives a *résumé* of the main results obtained by himself and other investigators with a view of elucidating the constitution of pyrroline, especially as regards—

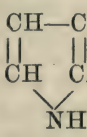
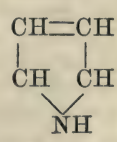
1. Its nature as an amine;
2. The combination of the carbon and nitrogen atoms in a closed chain;
3. The symmetric or asymmetric arrangement of the carbon and hydrogen atoms; and
4. The orientation of its derivatives.

Firstly. Pyrroline is a secondary amine, as Baeyer first supposed

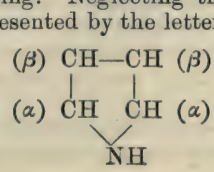
(*Ber.*, **3**, 517), although the non-formation of salts of the base, as also of a nitroso-derivative, present considerable difficulties in determining its nature. The formation of an acetyl-derivative by the direct action of acetic anhydride on pyrroline, put forward by R. Schiff as an argument in favour of its being a secondary amine is beside the point, as the compound described by Schiff is not the true acetyl-derivative, but a compound in which the acetyl grouping is directly combined with one of the carbon-atoms. The direct formation of di- and tetra-hydro-derivatives (Abstr., 1885, 1242), both of which are secondary amines, indicates that the present compound is of a similar constitution. This view is further supported by the reactions of potassium-pyrroline with ethyl chlorocarbonate, carbon oxychloride, and cyanogen chloride respectively, the two former of which yield tetrolcarbamides (Abstr., 1885, 809), and the last, a tetrolcyanamide corresponding with the diphenylcyanamide obtained from diphenylamine (Abstr., 1882, 599).

Secondly. The carbon and nitrogen-atoms form a closed chain. This view is supported by the formation of pyrroline from dibromomaleimide, of tetrachloropyrroline from dichloromaleimide, as also by the analogy of pyrroline to thiophen and furfuran, and the closely comparable reactions of pyrroline with those of phenol, as for instance with carbonic anhydride and carbon tetrachloride. But though the benzene compounds only form ketonic derivatives when treated with acid chlorides in presence of metallic chlorides, yet pyrroline forms such compounds by isomeric transformations of derivatives in which the acidic grouping is in combination with the nitrogen, into those in which these groupings are in combination with the carbon-atoms. Again, dinitropyridine is comparable in its reactions with picric acid.

Thirdly. As regards the more intimate constitution of pyrroline, the investigations made up to the present time are insufficient to show whether the hydrogen-atoms are symmetrically or assymmetrically situated with respect to the carbon-atoms, that is, it is impossible to decide between the alternative formulæ proposed by Baeyer (i) and Schiff (ii).

(i)  and (ii) 

Fourthly. A simple closed chain formula of pyrroline would indicate the formation of three possible isomeric mono-derivatives, according as the substituted grouping displaces a hydrogen-atom (i) in the NH grouping, in either of the CH groupings next to (ii), or removed from (iii) the NH grouping. Neglecting the first of these, there are the two alternatives represented by the letters α and β.



Of the derivatives known, the pyrrolinecarboxylic acid is undoubtedly an α-compound, as also are pyrryl methyl ketone and pyrrylglyoxylic acid obtained from it, whilst the dimethylpyrroline obtained from bone oil is an α-α-derivative. It is possible, however, that on further investigation pyrroline may present anomalies similar to those indicated by V. Meyer in the case of thiophen.

V. H. V.

Quinolineorthosulphonic Acid. By A. Claus and P. Küttner (*Ber.*, **19**, 925—926).—Salts of quinolineorthosulphonic acid, as distinguished from those of the para-acid, yield the ethereal salts of the acid with the halogen-derivatives of the hydrocarbons. Thus, with ethyl iodide, the silver salt forms ethyl quinolineorthosulphonate, $C_9H_6N\cdot SO_3Et$, which crystallises in tufts of colourless needles soluble in alcohol and ether, insoluble in water; it is readily reconverted into the acid. Another point of difference between the ortho- and the para-acids, is that the acid chloride of the former is readily obtained by the action of phosphoric chloride; it crystallises in needles which melt at 124°, and are slowly decomposed by water, whereas all attempts to prepare the acid chloride of the para-acid have hitherto been unsuccessful.

V. H. V.

Quinolineparasulphonic Acid. By A. Claus and P. Stegelitz (*Ber.*, **19**, 920—924).—The previous statement (Abstr., 1885, 560), as to the formation, not of ethereal salts of quinolineparasulphonic acid, but of the sulphobetaïnes, by the direct reaction of the silver salt of the acid with the alcoholic bromide, is confirmed. Thus *quinolineparasulphobenzylbetaïne*, $C_9H_6N\cdot SO_3\cdot C_7H_7$, obtained from benzyl bromide, crystallises in the monoclinic system ($a : b : c = 0{\cdot}841 : 1 : 0{\cdot}178$; $\beta = 123° 39'$) with 2 mols. H_2O. It is not converted into the sulphonic acid by any of the common saponifying agents. In presence of excess of acids, it forms very unstable salts; with iodine dissolved in potassium iodide, it yields a periodide of the composition $C_9H_6N\cdot SO_3\cdot C_7H_7,KI,I_3$, crystallising in blue, glistening crystals of metallic appearance; these when heated at 100° give off an atom of iodine, and at 200° melt with decomposition. The corresponding *ethyl* compound forms a periodide, $C_9H_6N\cdot SO_3Et,KI,I_3$, of similar appearance, but of a red tint, soluble in water, but with complete decomposition; with mercuric chloride, it gives a compound, $C_9H_6N\cdot SO_3Et,HgCl_2$, crystallising in long, colourless needles which melt at 250°. Similar metallic derivatives have also been obtained.

V. H. V.

Quinolinedisulphonic Acids and their Derivatives. By W. La Coste and F. Valeur (*Ber.*, **19**, 995—998).—These acids are obtained by heating quinolinemonosulphonic acid with twice its weight of Nordhausen sulphuric acid in sealed tubes at 250° for 18 hours, the two acids formed being separated by the difference in solubility in hot water of their barium salts, that of the α-acid being readily soluble.

α-Quinolinedisulphonic acid, $C_9NH_5(SO_3H)_2 + 3H_2O$, crystallises in clear yellow needles, very readily soluble in water, insoluble in

absolute alcohol. The *barium* salt crystallises with 3 mols. H_2O in colourless needles.

α-Hydroxyquinolinesulphonic acid, $OH{\cdot}C_9NH_5{\cdot}SO_3H + H_2O$, prepared by fusing the α-disulphonic acid with soda at 160° and decomposing the product with sulphuric acid, forms yellow flocks, sparingly soluble in cold water.

α-Dihydroxyquinoline, $C_9NH_5(OH)_2$, is prepared by fusing the disulphonic acid with five times the amount of soda at 260°. It crystallises in short, white needles, which soon oxidise and turn yellow on exposure to air, is readily soluble in ether, more sparingly in benzene, and forms stable salts with acids.

β-Quinolinedisulphonic acid, $C_9NH_5(SO_3H)_2 + 1\frac{1}{2}H_2O$, crystallises in white needles. The barium salt, with 2 mols. H_2O, forms a white amorphous powder. *β-Hydroxyquinolinesulphonic acid*,

$$OH{\cdot}C_9NH_5{\cdot}SO_3H + H_2O,$$

crystallises in yellow plates. *β-Dihydroxyquinoline* is mentioned, but not described. A. J. G.

2′ : 4′-Dimethylquinoline and the Synthesis of Cincholepidine and 4′-Phenylquinaldine. By C. Beyer (*J. pr. Chem.* [2], **33**, 393—425).—2′ : 4′-dimethylquinoline, $C_9NH_5Me_2$, described by Engler and Riehm (Abstr., 1885, 1246), is best prepared by saturating a cooled mixture of 120 grams of paraldehyde and 200 grams of acetone with dry hydrogen chloride; after two days a solution of 200 grams of aniline in 400 grams of strong hydrochloric acid is added. The whole is warmed for some hours on a water-bath, it is then distilled with steam to remove any condensation products of acetone, and the base, after being extracted in the usual way, is purified by conversion into the chromate. It is a colourless refractive oil, boiling at 264—265° (uncorr.), sp. gr. at 15° = 1·0611. The *platinochloride*, $(C_{11}NH_{11})_2,H_2PtCl_6$, forms lustrous, reddish-yellow needles (with water of crystallisation) melting at 229°; the *picrate* crystallises in yellow needles, sparingly soluble in alcohol; it melts at 190°. The *dichromate* forms splendid, long, yellowish-red needles, melting at 172°; the *zincochloride* and disulphate are also described. The *methiodide* and *ethiodide* form yellow needles melting at 225—226° and at 214° respectively. Both compounds, when treated with dilute caustic soda and exposed to air, yield dyes—probably cyanine compounds. The "*phthalone*," $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_{11}NH_9$, is obtained by heating the base with phthalic anhydride for several hours at 200°. The product is ground up, dissolved in strong sulphuric acid at 100°, and the solution poured into water; the dirty yellow flakes thus precipitated are crystallised successively from glacial acetic acid, benzene, and alcohol. It forms yellowish-red needles melting at 237—238°, rather readily soluble in acetone and chloroform. It has the properties of a valuable dye.

The *sulphonic acid* of the base, $C_{11}NH_{10}{\cdot}SO_3H$, is prepared by adding it slowly to three times its weight of fuming sulphuric acid, and then heating for some hours at 100—130°. It crystallises in

white, rhombic plates or flat needles, which do not melt at 300°. The *barium salt* forms slender needles. Other salts were prepared; they are mostly readily soluble.

Dimethylhydroxyquinoline, $C_{11}NH_{12}\cdot OH$, is obtained by gradually adding the sulphonic acid just described to six times the quantity of fused caustic soda. It is readily soluble in alcohol and ether, sparingly in water; it melts at 44°. The *platinochloride* (with 2 mols. H_2O) was prepared.

When a solution of the base in dilute sulphuric acid is boiled with chromic acid, a *lepidinecarboxylic acid*, $C_9NH_6\cdot COOH$, is obtained. The latter forms globular aggregates of microscopic needles, which melt at 240° and decompose at a slightly higher temperature with evolution of gas; it is soluble in hot water. It has strong acid and also basic properties, being readily soluble in dilute mineral acids. When carefully heated, it sublimes partly, the greater part, however, being carbonised. The *silver* salt forms a crystalline powder, very sparingly soluble in water, readily in ammonia and in dilute nitric acid. When the acid is distilled with lime, it is converted into 2′-methylquinoline (quinaldine), boiling at 235—238°. The acid must therefore have the constitution [2′ : 4′], a 2′ : 3′-acid having been already prepared by Friedländer and Göhring (Abstr., 1883, 1148). From this, the constitution of the base $C_{11}NH_{11}$, as given above is derived.

Lepidinecarboxylic acid is identical with Böttinger's aniluvitonic acid (Abstr., 1884, 320), and with an acid obtained by Pfitzinger from isatic acid and acetone.

Cincholepidine, C_9NH_6Me [Me = 4′], was prepared by saturating 30 grams of methylal and 30 grams of acetone with hydrogen chloride, adding 36 grams of aniline dissolved in 70 grams of concentrated hydrochloric acid, and warming the whole on a water-bath for some hours. It was then diluted, made alkaline, and distilled with steam. It boils at 253—255° (uncorr.), (compare Weidel, Abstr., 1882, 530). The yield of pure base is not good.

4′-Phenylquinaldine (Geigy and Königs, Abstr., 1885, 1236) was obtained in a similar manner from paraldehyde, acetophenone, and aniline.

These reactions are explained by assuming that the aldehyde and ketone first condense with formation of an unsaturated ketone (ethylidene acetone, CHMe : CH·COMe, methyleneacetone, CH : CH·COMe, &c.), and that this combines with the aniline with elimination of hydrogen and water. N. H. M.

Phenylisoquinoline. By S. Gabriel (*Ber.*, **19**, 830—836).—This is a continuation of the author's previous work on this subject (this vol., p. 266). By treating isobenzalphthalimidine in acetic solution with nitrous acid, *nitroisobenzalphthalimidine*, $C_6H_4<\begin{matrix}C(NO_2):CPh\\C(OH)=\!=\!=N\end{matrix}>$, is obtained; it forms small, yellow crystals, sparingly soluble in boiling alcohol, easily in boiling acetic acid, ether, &c. It begins to coagulate at 225°, and melts with partial decomposition at 245°. It dissolves in boiling soda solution with an orange coloration, and the

solution deposits the *sodium-derivative* in yellow needles. This derivative is so very soluble in water and alcohol that it was not obtained in a perfectly pure state, but when treated in alcoholic solution with methyl iodide, it yielded the *methyl ether*, $C_6H_4<\begin{matrix}C(NO_2):CPh\\-C(OMe):N-\end{matrix}>$. This forms flat, yellow crystals melting at 167—169°, moderately soluble in alcohol, easily in benzene, acetic acid, &c. When reduced with hydriodic acid and phosphorus, nitroisobenzal phthalimidine does not lose the nitro-group, as its isomeride, nitrobenzalphthalimidine, does, but yields *amidoisobenzalphthalimidine*, $C_6H_4<\begin{matrix}C(NH)_2:CPh\\-C(OH):N-\end{matrix}>$. This crystallises in yellow needles which melt at 190°, and are easily soluble in acetic acid and boiling alcohol, sparingly in ether and chloroform. When treated with phosphoric oxychloride, the nitroimidine yields *phenylchloronitroisoquinoline*, $C_6H_4<\begin{matrix}C(NO_2):CPh\\--CCl:N--\end{matrix}>$, crystallising in yellow needles or prisms melting at 155—156°. It has an odour resembling that of musk, and is sparingly soluble in alcohol, easily in chloroform, ether, &c. When boiled with hydriodic acid, this substance yields a base, *phenylamidoisoquinoline*, $C_6H_4<\begin{matrix}C(NH_2):CPh\\--CH:N--\end{matrix}>$; this crystallises in yellow scales or needles, which dissolve easily in the ordinary solvents and melt at a little above 100°. The *hydrochloride*, *platinochloride*, and *hydriodide* are described.

Phenylchloroisoquinoline, [Ph : Cl = 3 : 1], melting at 77—78°, and previously described (*loc. cit.*), when treated with sodium ethylate yields *phenylethoxyisoquinoline*, $C_6H_4<\begin{matrix}CH:CPh\\C(OEt):N\end{matrix}>$. It is a feeble base, easily soluble in the ordinary solvents, and crystallises in colourless needles melting at 45—46°. The *hydrochloride* forms needles which are decomposed by water, the *platinochloride* a reddish, granular precipitate.

The above formulæ are based on the assumption that isobenzylphthalimidine has the formula

$$C_6H_4<\begin{matrix}CH:CPh\\C(OH):N\end{matrix}>, \text{ and not } C_6H_4<\begin{matrix}Ch:CPh\\-CO\cdot NH-\end{matrix}>,$$

but the author considers this can still hardly be looked on as fully established. L. T. T.

Flavaniline. By O. Fischer (*Ber.*, **9**, 1036—1039; compare Abstr., 1882, 1066; 1883, 600; 1885, 400). — *Flavoquinoline*, $C_9NH_5Me\cdot C_9NH_6$, is prepared by mixing flavaniline, nitrobenzene, and glycerol with concentrated sulphuric acid, heating until action commences, and, after the first violent reaction has ceased, again heating to gentle boiling for three hours. It forms colourless, seemingly rhombic crystals, melts at 138°, and has powerfully basic properties; its salts with mineral acids show a blue fluorescence when dissolved. As regards its constitution, the one quinoline

nucleus has a methyl-group in the 4′ position, and is united at 2′ to the 3 position of the other quinoline-group. The methiodide, $C_{19}H_{14}N_2MeI$, crystallises in slender, yellowish needles.

When orthamidacetophenone is treated with acetone and aqueous soda, it yields dimethylquinoline (b. p. 260—262°). With aldehyde or paraldehyde, it gives a very small amount of a methylquinoline. The synthesis of flavoline can be effected by dissolving acetophenone and orthamidoacetophenone in dilute alcohol, adding a small quantity of 10 per cent. aqueous soda, and heating on the water-bath with frequent agitation for several hours. The author's earlier assumption that flavoline is α-phenyl-γ-lepidine is thus fully confirmed.

Flavaniline seems to be α-paramidophenyl-γ-lepidine, inasmuch as it is abundantly formed by heating orthamidoacetophenone and paramidacetophenone with zinc chloride. The small yield of flavaniline obtained on heating orthamidacetophenone with zinc chloride, which led the author to regard it as an ortho-compound, is most likely due to intramolecular change.

Flavaniline is but little affected by treatment with hydrochloric acid and tin or zinc, but is reduced when treated with sodium and alcohol, being converted into a colourless base whose hydrochloride crystallises in colourless cubes. A. J. G.

Cinchonidine in Commercial Quinine Sulphate. By A. J. Cownley (*Pharm. J. Trans.* [3], **16**, 797). With regard to the statement made by De Vrij (Abstr., 1885, 302) that commercial quinine sulphate contains above 5 per cent. of cinchonidine sulphate, the author points out that such is the case only in inferior kinds of quinine sulphate; for out of 28 samples of quinine sulphate examined by a very delicate method, some were found to contain none, only two 5 per cent. or over, whilst the average was 2·04 per cent. of cinchonidine sulphate. Hence, as De Vrij worked with brands of the highest repute, it is inferred that the method employed is in fault.

D. A. L.

Reaction of Atropine with Mercurous Salts. By A. W. Gerrard (*Pharm. J. Trans.* [3], **16**, 762.) When mercurous chloride, nitrate, or acetate are warmed with atropine in the presence of water, the metallic salt is decomposed, with formation of mercurous oxide and a salt of atropine. No compound of atropine with the mercurous salt is formed, as is the case with mercuric salts (compare this vol., 285, 397). The reaction is aided by the addition of alcohol to dissolve the atropine, and it goes better with soluble than with insoluble mercurous salts. By suitable manipulation, the reaction with mercurous nitrate can be obtained with less than 0·001 gram of atropine, and is, therefore, a delicate test for the alkaloïd.

D. A. L

Cocaïne and Atropine. By Fluckiger (*Pharm. J. Trans.*, [3], **16**, 800).—With regard to the instability of cocaïne, its alkalinity and its decomposition by water, the author confirms some of his own results (this vol. p. 397), and some of those of other observers (next Abstr.; this vol., pp. 84, 388, 480, &c.). He has, moreover, observed that atropine is decomposed by prolonged heating with

water in a closed tube at below 100°. By adding a solution of potassium permanganate to a solution of cocaïne hydrochloride, both of suitable strength, a characteristic precipitate of cocaïne permanganate is obtained (Giesel, *Pharm. Zeit.*, Berlin, 1886, 132). D. A. L.

Cocaïne Benzoate. By B. H. Paul (*Pharm. J. Trans.* [3], **16**, 817—818).—A light crystalline powder purporting to be cocaïne benzoate, on examination, proved to be benzoylecgonine. The author has, however, succeeded in obtaining acicular crystals of cocaïne benzoate. A description is given of the preparation of benzoylecgonine by heating cocaïne and water in a closed tube. The resulting liquid is only very faintly acid, when pure cocaïne is used, but with impure cocaïne it is decidedly acid, and on evaporation it deposits crystals of benzylecgonine. Air-dried benzylecgonine retains water and melts below 100°, but when it is dried over sulphuric acid, the crystals become opaque and melt above 100° (compare Abstr., 1885, 1249). The author now finds that when this substance is heated with strong hydrochloric acid it does yield benzoic acid (compare this vol., pp. 84, 480; and Abstr., 1885, 997, 1250). D. A. L.

Hydrastine. By A. B. Lyons (*Pharm. J. Trans.* [3], **16**, 880—881; compare Abstr., 1885, 607, 675).—Pure sulphuric acid dissolves pure hydrastine, producing a solution with only a slight tinge of yellow. On heating, it changes to deep bluish-purple; this observation differs from those of previous investigators (*loc. cit*). In the presence of nitric acid, the change is different; with a trace only, the solution is yellow; when the quantity is 1 in 1000, the solution is orange-red, whilst with larger proportions it is orange or pale red. Pure nitric acid produces a solution of a permanent orange colour; on the addition of water a precipitate forms, and an intense blue fluorescence is developed. With concentrated sulphuric acid and manganic oxide, hydrastine gives rise to an orange colour, changing successively to cherry-red, carmine, yellowish-red, and ultimately pale-orange-yellow. Under similar conditions, berberine gives violet, chocolate-brown, and orange-red, and strychnine gives indigo, violet, and red. Similar colour reactions are given if the manganic oxide is replaced by either barium iodate, potassium dichromate, or potassium permanganate. Potassium dichromate produces a precipitate in solutions of hydrastine (*loc. cit.*, 607), and when this precipitate is touched with concentrated sulphuric acid, it immediately assumes a transient bright-red colour; this reaction distinguishes hydrastine from strychnine and gelseminine. The most striking reaction is the production of an intense blue fluorescence when hydrastine is digested with dilute sulphuric acid and manganic oxide, or when a solution of hydrastine is treated with a small quantity of dilute sulphuric acid and a few drops of dilute permanganate; excess of permanganate destroys the alkaloïd completely and the fluorescence also disappears. Alkalis neither develop nor increase the fluorescence. The fluorescent substance is soluble in water and alcohol, very insoluble in ether or chloroform. Solutions of hydrastine hydrochloride are more or less

fluorescent if the salt has been dried or exposed for some time to a moderate heat. D. A. L.

Ptomaïnes and Leucomaïnes. By A. Gautier (*J. Pharm.* [5], **13**, 354—360, and 401—409; compare Abstr., 1885, 676).—The author gives a *résumé* of the work done on these alkaloïds. From the muscle of large animals, he has succeeded in obtaining five new alkaloïds (leucomaïnes), perfectly definite in composition and crystalline form, which, when administered to animals, act more or less powerfully on the nerve centres, inducing sleep, and in some cases causing vomiting and purging, in a manner similar to the alkaloïds of snake poison, but less powerfully than the ptomaïnes. These bases are formed during life and occur in the urine, saliva, venom, and various glandular secretions; but the author has more particularly studied their occurrence in muscle.

Xanthocreatinine, $C_5H_{10}N_4O$, is the most abundant of the bases obtained from muscle. It consists of light sulphur-yellow spangles, with a slightly bitter taste. The crystals are very soluble in water and soluble in hot alcohol. They slowly blue reddened litmus-paper and reddened the blue paper. The hydrochloride is obtainable. The platinochloride is very soluble, and crystallises in long sheaves. The aurochloride is difficult to obtain in the crystalline form. The substance closely resembles creatinine. This resemblance, together with its yellow colour, is indicated in its name.

Crusocreatinine, $C_5H_8N_4O$, is decidedly alkaline to test-paper, and gives a soluble non-deliquescent hydrochloride, and a soluble platinochloride. The slightly soluble aurochloride occurs in crystalline grains. This base neither precipitates zinc from its acetate nor mercury from its nitrate, but it precipitates alumina from alum solutions. It strongly resembles creatinine.

Amphicreatinine, $C_9H_{19}N_7O_4$, occurs in small quantity only. It is a feeble base, forming a non-deliquescent crystalline hydrochloride. Its platinochloride is soluble in water, insoluble in alcohol, and forms lozenge-shaped plates. Its aurochloride forms very soluble, microscopic, hexahedral, and tetrahedral crystals.

Pseudoxanthine, $C_4H_5N_5O$.—The alcoholic mother-liquors from the preceding compounds are freed from alcohol, the residue is taken up with water, and treated with copper acetate in slight excess. On heating, a precipitate is obtained from which the copper is separated by means of hydrogen sulphide. On filtering the boiling solution, a light sulphur-yellow powder is obtained. This substance readily forms a very soluble hydrochloride. It is similar to xanthine, except that it is slightly more soluble, and there is a little difference in the crystalline form. The author has also obtained two other bases of the composition $C_{11}H_{24}N_{10}O_5$ and $C_{12}H_{25}N_{11}O_5$ respectively, whose reactions show their close relation to creatinine. During the writing of this paper, Brieger has described a very poisonous leucomaïne, of the composition $C_6H_{15}NO_2$, obtained from poisonous mussel, which he calls *mytilotoxine*. J. T.

Gelatin. By E. Buchner and T. Curtius (*Ber.*, **19**, 850—857).—Gelatin, swollen with a small quantity of water, was treated with absolute alcohol and heated on a water-bath for 20 hours, during which time hydrogen chloride was passed into it. The alcohol was then distilled off and the residue kept for some weeks over soda-lime to remove the excess of acid, after which it was treated in small quantities with sodium nitrite. The crude product was distilled with steam, and afterwards in a vacuum. In this way a pure *diazo-compound*, $C_5H_6N_2O_3$, was obtained. It forms a lemon-yellow oil, having a peculiar odour, and boils almost without decomposition at 141—142° under 717 mm. pressure. It has the characteristic properties of fatty diazo-compounds. When boiled with strong potash solution, it slowly decomposes with separation of ethyl alcohol and carbonic anhydride. Zinc-dust and acetic acid reduce it readily with formation of a hydrazine, and this, when further reduced, yields ammonia and a base. When an ethereal solution of the diazo-compound is treated with iodine, it is converted into *diazovinylamine*, $CI_2{:}CH{\cdot}NH_2$. This crystallises from water in small, slightly yellow prisms, very sparingly soluble in ether, more readily in hot alcohol and water. Sulphuric acid dissolves it unchanged. When heated, it becomes yellow at 170°, and melts with decomposition at 192°.

The formation of alcohol by the action of alkali on the diazo-compound, makes it probable that the latter is the ethyl salt of a diazo-fatty acid, having the constitution $CHN_2{\cdot}CH(OH){\cdot}COOEt$.

When the product obtained by the action of alcoholic hydrochloric acid on gelatin is treated with alkali, a basic substance is formed, having an intense, repulsive odour. It is very unstable, and gives off carbonic anhydride very readily.

Albumin, when treated with alcoholic hydrochloric acid, gave results similar to those obtained with gelatin. This is fresh proof of the analogy between the two substances in their chemical properties. Löw has suggested that albumin is a condensation-compound of aspartic aldehyde, and more recently Schützenberger, by treating albumin with baryta, obtained a compound which he described as leucein (*Compt. rend.*, **101**, 1267). The simplest formula for this compound, namely, $C_4H_7NO_2$, is also the formula of aspartic aldehyde. N. H. M.

Composition of Albumin. By P. W. Latham (*Brit. Med. J.*, 1886, 629—636).—A discussion of the constitution of this compound and of the possible manner in which it may be built up from more simple groups of elements.

Edible Bird's-nest. By J. R. Green (*J. Physiol.*, **6**, 40—45).—The substance of which the edible bird's-nest is composed, named by Krukenberg *neossine* (see this vol., p. 481), resembles mucin very closely, the chief differences being:—(1.) The nest is insoluble in 5 per cent. HCl and in dilute alkalis, whilst mucin is soluble in both. (2.) Mucin in solution is precipitated by acetic acid, while the nest solution only becomes opalescent. (3.) The nest substance is slowly digested by pepsin, whilst mucin is indigestible. (4.) Mucin, in solution in soda, yields to ether a substance coloured green by ferric

chloride; the nest material does not. This substance is thus an animal product, and it is hardly open to doubt that it is the result of the activity of the glands described by Bernstein (*Journ. Ornithologie*, 1859, 111), as being remarkably developed in the nest-building season, and as atrophying immediately afterwards. W. D. H.

A New Ingredient of the Liver. By E. Drechsel (*J. pr. Chem.* [2], 425—432).—Fresh liver was washed with water, finely divided, and mixed with 2—3 volumes of absolute alcohol. The next day, the liquid was poured off, and the substance treated with fresh alcohol until completely extracted. The alcohol was then evaporated at 40—50°. The residue so obtained, when subjected to a treatment (described in detail) with solvents, yielded a new compound, *jecorin*, $C_{105}H_{185}N_5SP_3Na_2O_{46}$; this is a light substance of an earthy appearance, and can easily be rubbed to a fine powder; when dry, it is very electric. It has a great attraction for water. Absolute ether dissolves it sparingly, but wet ether dissolves it, forming a slightly opalescent solution. When an aqueous solution of jecorin is evaporated over sulphuric acid, an amorphous, gum-like residue is obtained, which no longer dissolves in wet ether. It is precipitated from its aqueous solution by addition of concentrated solutions of salts. When a solution of the substance is boiled in presence of a silver salt and ammonia, it acquires a splendid port wine colour; this is perhaps due to the reduction of the silver salt. Jecorin also reduces Fehling's solution and an alkaline solution of potassium ferricyanide when boiled with them. When boiled with caustic soda, and the product treated with acid, hydrogen sulphide is evolved, and the solution is found to contain sulphuric (?) and phosphoric acids. Boiling hydrochloric acid decomposes it with formation of stearic acid.

Further experiments will have to be made to show whether jecorin is a single substance. N. H. M.

Precipitation of Peptones. By S. H. C. Martin (*Proc. Physiol. Soc.*, 1886, 5—6).—In addition to Hofmeister's ferric acetate method of precipitating all proteïds except peptones from a solution, another method is to saturate the liquid with sodium magnesium sulphate; this salt completely precipitates albumins, globulins, albuminates, and albumoses; but all peptones remain in solution. Heynsius stated (*Pflüger's Archiv*, **34**, 330) that saturation with normal ammonium sulphate precipitates all proteïds including peptones; whereas Kühne (*Verhandl. Naturhist.-Med. Vereins, Heidelberg*, **3**) says that peptones are left in solution, and that the peptones used by Heynsius were in reality albumoses. On this statement of Kühne's, Wenz and Pollitzer have based their experiments. The present research was directed to settle this disputed point, and it was found that ammonium sulphate does precipitate pure peptones, the greater part of them readily, the small remaining quantity by shaking the liquid with excess of the salt for a short time to ensure perfect saturation. Gelatin peptones are likewise completely precipitated by saturation with this salt. W. D. H.

Conversion of Hæmoglobin into Methæmoglobin. By G. Hayem (*Compt. rend.*, **102**, 698—700).—The following substances have the power of converting hæmoglobin into methæmoglobin:—Nitrites (amyl and sodium), chlorates (potassium and sodium), ferricyanides (potassium and sodium), potassium permanganate, pyrogallol, kairine, thalline, quinol, catechol, osmic acid, iodine, bromine, terebenthene, and ether.

Amyl nitrite and kairine differ from the other substances in that they convert the hemoglobin into methæmoglobin without any other alterations of the corpuscles or the serum. Most of the other substances destroy the corpuscles more or less completely. The ferricyanides, however, act only on dissolved hæmoglobin; they exert no action on pure blood, and therefore can be administered in considerable doses without producing any methæmoglobin. C. H. B.

Hæmoglobin and Methæmoglobin Crystals of Rodents. W. D. Halliburton (*Proc. Physiol. Soc.*, 1886, 2—4).—The three animals in which hæmoglobin is stated to crystallise in six-sided plates are the mouse, hamster, and squirrel. Hamster's blood has not been examined in this research; the crystalline form of mouse's hæmoglobin was found to be rhombic needles not hexagons. Squirrel's hæmoglobin crystallises in six-sided plates. They remain dark when placed between crossed Nicols; this is in favour of their being true hexagons, instead of being rhombic plates with "hexagonal habit," or twins composed of adjacent parallelograms or triangles. The diagnostic shape of the interference figures seen in convergent polarised light could not be used as a confirmatory test as to which division of crystals they belonged; because on account of the small size and extreme tenuity of the crystals, neither rings nor cross were seen. The difference in crystalline form is due to some property inherent in the hæmoglobin itself, and not to any external agency in the blood, since it crystallises in its special form from the serum, the plasma, and from a fluid consisting of serum *plus* the dissolved stromata of the corpuscles from the blood of other animals. The hexagonal constitution of squirrel's hæmoglobin can be broken down by repeated recrystallisation, the crystals finally obtained being a mixture of rhombic needles and tetrahedra. The reverse experiment of mixing the hæmoglobin from the rat and guinea-pig (which crystallise in rhombic needles and tetrahedra respectively) and then allowing crystallisation to take place, yielded no needles or tetrahedra, but rhombic crystals simulating hexagons. The most probable theory of these differences in crystalline form is that they are dependent on the varying amount of water of crystallisation present (Hoppe-Seyler), in fact that different hydrates of oxyhæmoglobin exist. A simple method of preparing methæmoglobin crystals for microscopic examination is as follows: shake a few c.c. of defibrinated blood with a few drops of amyl nitrite for about a minute; a drop of the mahogany-coloured liquid so formed when placed on a slide yields in a few seconds an abundant crop of crystals. In the guinea-pig these are tetrahedra; in the rat and squirrel they have the same form, namely, a mixture of hexagons and rhombic prisms, the former greatly predominating. W. D. H.

Hæmatin and Bile Pigments. By C. A. MacMunn (*J. Physiol.*, **6**, 22—39).—An easy method of procuring hæmatin is as follows:—Blood clot is extracted with rectified spirit containing pure sulphuric acid (1 in 17), the solution filtered, diluted with an equal amount of water, and agitated with chloroform. The chloroform, which assumes a reddish-brown colour, is separated, filtered, and washed with water to remove the acid. The chloroform is evaporated, when the hæmatin remains as a dark-brown pigment which dries up to a bluish-black powder. If the chloroform solution is allowed to remain for a few hours, crystals of hæmatin, resembling in shape and colour those of hæmin, separate out.

The bile of carnivorous animals is free from absorption-bands; with the bile of the sheep and ox, however, a three- or four-banded spectrum is sometimes obtained; biliverdin is a bandless pigment, and these bands are due to the presence of another pigment called cholo-hæmatin. It may be thus separated: an ethereal extract of bile is evaporated and the residue taken up with chloroform, which is washed in a separating funnel with water. On evaporating the chloroform, a dark-green pigment with musky smell is left. It is regarded as a hæmatin-derivative; its spectrum suggests a mixture of alkaline hæmatin and hæmochromogen, and it is probably an intermediate stage in the formation of biliverdin. In bile obtained from four cases of biliary fistula in man, the chromogen of a colouring matter very similar to febrile urobilin and stercobilin was found, also a small quantity of biliverdin, and the chromogen of biliverdin, but no bilirubin. Spectroscopic examination of urobilin and stercobilin in various solvents shows, however, that the two pigments are not identical. W. D. H.

Hæmatoporphyrin. By C. A. MacMunn (*Proc. Physiol. Soc.*, 1886, 1—2).—Hæmatoporphyrin occurs in the peculiar streak on the dorsal surface of the earth-worm. It gives without any treatment the four-banded spectrum of neutral hæmatoporphyrin, and from it acid and alkaline hæmatoporphyrin can be obtained. W. D. H.

Physiological Chemistry.

Diastatic Action of Saliva. By R. H. Chittenden and H. E. Smith (*Chem. News.*, **53**, 109—111, 122—124, 137—138, 147—148, 161—163, 173—175).—For the purpose of testing the diastatic action of saliva quantitatively, a 1 or 2 per cent. solution of starch was exposed to the action of the saliva at 40° C. for half an hour, and the reducing substances formed were in all cases calculated as dextrose by Allihn's (*Zeit. anal., Chem.* **22**, 248) method. The action of a ferment is not proportional to its amount until its solution is much diluted; when the dilution of the saliva is as 1:50 or 100, the diastatic action can be taken as a measure of the amount of ferment

present. The normal alkalinity of 15 samples of saliva reckoned in terms of sodium carbonate was 0·097 per cent. When this is neutralised with 0·2 per cent. hydrochloric acid, its diastatic action is much increased, especially when the dilution is 1 : 50 or 100: but the difference is still pronounced when the dilution reaches 1 : 2000. There appears, however, to be no proportional relation between natural variations of alkalinity and diastatic action, although the addition of sodium carbonate to neutral saliva retards and finally stops the action of ptyalin in proportion to the amount added; this occurring especially readily in more dilute solutions. This is not due to simple dilution, but to the thereby diminished percentage of proteïd matter, which in the less diluted saliva possibly combines with the carbonate; and such proteïd compounds have no effect on the ferment. Neutral peptone, on the contrary, has a distinctly stimulating effect on the activity of neutral saliva; and when proportionate amounts of peptone and sodium carbonate are added, the destructive action of the latter is prevented, an alkaline proteïd substance being probably formed. The influence of free acid and of acid proteïd on the activity of ptyalin is important, in view of the rapid passage of the salivary secretions into the stomach. That gastric juice does destroy ptyalin has been shown by Langley (*J. Physiol.*, **3**); the present research was directed to determining quantitatively the particulars of such action; the tropæolin test being used for the detection of free acid. As a mean of eight determinations, 20 c.c. of neutralised saliva were found to contain proteïds capable of combining with 7·74 c.c. of 0·1 per cent. hydrochloric acid, a result showing on comparison with similar experiments with peptones, either that the combining power for acid of saliva proteïd and peptone is different, or that much acid is used up in reacting with the alkaline phosphates present in saliva. When the proteïd matter present is saturated with acid, the saliva has greater diastatic power than when it is simply neutralised. Small percentages of acid peptone act similarly, but beyond a certain point (when the amount of combined acid is over 0·006 per cent.), acid proteïds retard and finally destroy the action of the ferment. A minute trace of free acid in dilute saliva still further increases diastatic activity, but 0·003 per cent. of free hydrochloric acid stops it. W. D. H.

Formation of Hydrochloric Acid in the Stomach. By E. Frerichs (*Bied. Centr.*, 1886, 285).—The author found that in 10 to 15 minutes after the introduction of distilled water into the stomachs of men and dogs, traces of hydrochloric acid were found; in 35 to 45 minutes the maximum is reached. This does not agree with the observation of van der Velden that the acid is not perceptible until $1\frac{3}{4}$ to 2 hours after a meal. J. F.

The Blood of Decapod Crustacea. By W. D. Halliburton (*J. Physiol.*, **6**, 300—335).—The crab, lobster, fresh-water crayfish, and sea-water crayfish, were the animals employed.

In addition to hæmocyanin, a colouring matter first described by Fredericq, associated with a proteïd, and containing copper, the blood

plasma contains a red pigment, soluble in alcohol, which gives all the tests of a lipochrome, and is identical with the red pigment, tetronerythrin, which occurs in the liver and shell of these animals. It gives a faint absorption-band in the region of the F line. Among other extractives, a small amount of urea is present. The salts resemble those of the water in which these animals live, and are more abundant in sea-water than in fresh-water animals. The blood is always faintly alkaline; it clots immediately it is drawn, but coagulation can be prevented by very large quantities of neutral salts, or by cold. The clot is not the so-called plasmodium of coherent cells, as described by Geddes and others, but is due to the formation of a substance almost indistinguishable from vertebrate fibrin, in which the cells are entangled. Its formation is shown to be due to a ferment action upon a proteïd fibrinogenous substance, which is in life dissolved in the blood plasma. The ferment is derived from the amœboid corpuscles of the blood, and is identical with the fibrin ferment of shed vertebrate blood. After the separation of the clot, the only proteïd in the serum is hæmocyanin, which takes the place of the hæmoglobin of vertebrate blood. It is blue when oxidised, but shows no absorption-band; colourless when reduced. It is a globulin, being precipitated by a heat of 65°, by saturation with neutral salts, or by dialysis. W. D. H.

Cellulose in Protozoa. By W. D. Halliburton (*Quart. J. Mic. Sci.*, 1885, 445—447).—*Ophrydium versatile* is a ciliated protozoa, which grows in colonies exuding a common coalescent mucilaginous investing matrix or zoocytium. This material, when purified by washing in cold and hot water, dilute hydrochloric acid, dilute caustic potash, alcohol, and ether, was found to consist of cellulose. It differs from vegetable cellulose in being less easily converted into sugar, in which it resembles tunicin. Tunicin gives, however, a pale blue, this substance a brown colour with iodine. This shows that cellulose is not limited among animals to the family of tunicates; its coexistence with chlorophyll, another vegetable product in the same animal, is also noteworthy. W. D. H.

Therapeutic Action of Urethane. By A. Mairet and Combemale (*Compt. rend.*, **102**, 827—829).—In cases of mental derangement in which the brain has undergone organic alteration, urethane has no hypnotic effect, but in cases of functional mental derangement of various kinds the hypnotic action of the urethane is well marked, provided that the insomnia is not connected with too intense mental agitation. In all cases in which this action of urethane was observed, nutrition had been disturbed, and the badly nourished nervous cellules were enfeebled. It would seem, therefore, that the urethane has a direct action on the nervous tissue.

The hypnotic action of urethane is not so great as that of chloral, opium, &c., but it can be employed in cases where these drugs are not available. It is given in doses of 2—5 grams, and if the maximum dose is given at first and does not produce the desired result, it is useless to continue the administration. After a few doses, the efficacy

of the urethane diminishes considerably, and it is necessary to discontinue its administration for a few days in order to obtain the maximum effect. C. H. B.

Physiological Action of Zinc Sulphate. By — Lepetit (*J. Pharm.* [5], **13**, 360—362).—By mistake, instead of Glauber's salt zinc sulphate was administered as medicine to many inmates of a prison, the only difference at first observed being the addition of emeto-cathartic effects in addition to simple purgation. A dose of 60 grams resulted in the death of a patient. Zinc was found in the stomach and its contents, the liver, the spleen, and the substance and contents of the intestines. J. T.

Elimination of Carbonic Oxide after Partial Poisoning. By N. Gréhant (*Compt. rend.*, **102**, 825—827).—Further experiments confirm the author's previous conclusion that after partial poisoning by carbonic oxide this gas is entirely eliminated in the process of respiration, and is not converted into carbonic anhydride in the organism. The fact that Kreis found very little carbonic oxide in the products of respiration under similar circumstances is probably due to defects in his method of estimating this gas. C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

A Soluble Urea Ferment from the Torula Ureæ. By A. Sheridan Lea (*J. Physiol.*, **6**, 136—142).—Musculus has shown (*Compt. rend.*, **78**, 132; this Journal, 1876, i, 952) that a ferment is separable from the *Torula ureæ*. The present experiments show that this ferment (which is obtainable by precipitation of the cells by alcohol, and subsequent extraction with water) is not present in the liquid part of the urine in which alkaline fermentation is going on; the alcoholic precipitation of urine, freed from organisms by filtration through a porous cell, being inactive in producing decomposition of urea. The invertin of ordinary yeast resembles the urea ferment of the *Torula ureæ*, inasmuch as that though soluble, and capable of being isolated by approximate methods from the dead cell substance, it is not present in the fluid surrounding the cells during the progress of the change which they produce. This is probably due to the fact that ferments being non-diffusible, are unable to pass from the protoplasm of the torulæ through its surrounding investment of cellulose. W. D. H.

Papaïn Digestion. By S. H. C. Martin (*J. Physiol.*, **5**, 213—230).—Papaïn is shown to be a proteolytic ferment, which acts very similarly to trypsin. Experiments performed with fibrin and coagulated white of egg showed that some degree of digestion occurs when the liquid is faintly acid (0·05 per cent. HCl); the presence of more

acid than this hinders the action of the ferment. Digestion takes place actively only in neutral or in alkaline solutions (0·25 per cent. sodium carbonate); it occurs most readily at a temperature between 35° and 40°. The results of digestion are peptones, leucine, and tyrosine, and an intermediate globulin-like substance, similar to that formed in pancreatic digestion (compare this vol., p. 74).

W. D. H.

Nature of Papaïn and its Action on Vegetable Proteïd. By S. H. C. Martin (*J. Physiol.*, **6**, 336—360).—The ferment in papaw juice is associated with an albumose, and to the reactions previously stated by Wurtz (Abstr., 1880, 58, 750), the following are added; the solution gives a biuret reaction, and it is precipitated from a neutral solution by sodium magnesium sulphate, the precipitate still being active. It is not precipitated by magnesium sulphate or sodium chloride alone, as globulins are. It is soluble in glycerol, and if precipitated from this solution by alcohol, the filtrate has no proteolytic power. The kind of albumose is one nearly akin to the protalbumose of Kühne and Chittenden, and is called α-phytalbumose. Papaw juice also contains a milk-curdling ferment.

The proteïds present in papaw juice were found to be as follows:—(1.) Globulin, resembling serum globulin in its most important properties. (2.) Albumin. (3.) β-Phytalbumose precipitated almost completely by heat, by saturation with neutral salts, but not by dialysis. It differs from the heteroalbumose of Kühne and Chittenden, by not being precipitated by dialysis, by copper sulphate, or by mercuric chloride. (4.) α-Phytalbumose; soluble in cold or boiling water; not precipitated by saturation with neutral salts, except in an acid solution. This is the vegetable peptone referred to by Vines (*J. Physiol.*, **3**) as hemialbumose. It differs from the protalbumose of Kühne and Chittenden by its non-precipitation by sodium chloride or by copper sulphate. Both these albumoses give the biuret reaction. No peptones occur in the juice, but leucine and tyrosine are present.

By a series of digestion experiments carried out on each of these proteïds by papaïn in a neutral liquid, it was found that both the globulin and albumin are changed into β-phytalbumose, and that this becomes a peptone-like substance, and forms leucine and tyrosine. The α-phytalbumose becomes a similar peptone-like substance, leucine and tyrosine being formed. This peptone-like substance resembles the deuteroalbumose of Kühne and Chittenden, except that a solution of it when rendered acid by acetic acid in the presence of sodium chloride does not become cloudy on warming. No true peptones are formed.

Probably digestion in the plant itself is very slow, as much more liquid was used in the experiments than is present in the juice. The albumose forms probably the circulating proteïd in the plant.

W. D. H.

Emission of Oxygen by Plants observed with the Microspectrum. By N. Pringsheim (*Bied. Centr.*, 1886, 253—254.)—Engelmann has demonstrated a function of chlorophyll, that under the influence of light and especially of rays of certain wave-lengths which are absorbed by it, the grains of chlorophyll decompose carbonic

anhydride into carbon and oxygen. He employs bacteria as reagents; a drop of water containing them is brought under the microscope, they at once gather round the edges of the cover glass where a supply of oxygen can be obtained; if a few green plant cells in full activity be placed in this drop of water, the bacteria will gather round the chlorophyll grains, showing that oxygen is being disengaged: if a spectrum be then thrown on them, it will be found that the greatest activity is developed between the lines B and C.

The author has studied this part of the subject for two years, and has repeated Engelmann's experiments with many variations; he thinks dissociation of carbonic anhydride is a function of the colourless cell protoplasm, and that the chlorophyll merely protects this from the hurtful influence of too strong a light. He considers the experiments with the spectrum untrustworthy, and that the subject requires further investigation. J. F.

Constituents of Milk-sugar in Plants. By A. Müntz (*Compt. rend.*, **102**, 681—684).—The author has already shown that galactose, identical with that obtained from milk-sugar, is a product of the splitting up of vegetable substances, such as gums, pectic bodies, &c. (this vol., p. 575). He has redetermined the proportion of pectic substances, gums, &c., in various vegetable products which are largely used as food for man and animals. The pectic substances were estimated in the form of pectic acid, which was the same in all cases, but the gums showed considerable differences, indicating the existence of distinct chemical species. The gums derived from fruits have as a rule a lævorotatory power approaching that of gum arabic, whilst those from leguminosæ have a strong dextrorotatory power.

Wheat grains contain 0·5 per cent. of pectose, and 0·5—1·0 of gum; rye, 0·7 of pectic bodies and 2·3 of gum; barley, 0·9 of pectic bodies and 2·8 of gum. Some leguminous seeds contain chiefly pectic substances, whilst in others gums are present in the larger proportion. White haricots, broad beans, and horse beans contain 2—4 per cent. of pectic substances, whilst other leguminous seeds, especially those which are oleaginous, contain a large proportion of the gum which the author has described under the name of galactin. Cider apples contain 0·8 per cent. of pectose and 0·5 of gum; plums, 0·5 of pectose, 1·2 of gum; grapes, 0·6 of pectose and 0·4 of gum. Roots and tubers are usually rich in pectic substances, mainly pectose, and always contain gum, the average proportions being carrots 1—2 per cent. of pectic substances and 0·5 of gum; beetroot, 0·5—1·0 of pectic substances, 0·6 of gum; artichokes, 0·6 of pectic substances, 0·5 of gum; potatoes, 0·6 pectic substances and 0·8 of gum. Cabbage-leaves contain 0·6—1·2, and chicory leaves, 0·5—1·0 of pectic acid. With forage the following results were obtained: green lucerne, pectic substances 0·8—1·3, gum 1—2; seed-grass, 1·1—4·5 pectic substances, 1·3 of gum; wheat-straw, 1—2 pectic substances, 0·5 of gum; culm of leguminosæ, 1—6 of pectic substances. Gums are also always found in fermented beverages.

Experiments were made by feeding cows on a diet containing a known proportion of pectic bodies and gums, and measuring the yield

of milk. It was found that in all cases the quantity of the constituents of milk-sugar in the food was more than sufficient to account for all the milk-sugar in the milk given, but no exact balance between the two quantities could be established. C. H. B.

Apricot, Peach, and Walnut Oils. By T. Maben (*Pharm. J. Trans.* [3], **16**, 797—800).—These oils to some extent resemble almond oil. Apricot oil is of a clear pale yellow colour, with a distinct odour of hydrocyanic acid and amygdalaceous flavour. Peach oil is similar, but more intense in colour, odour, and taste. Walnut oil is well known. The following table illustrates the behaviour of these oils under certain conditions.

	Drying oil.			Non-drying.
	Apricot oil.	Peach oil.	Almond oil.	Walnut oil.
Sp. gr. at 15·5°	0·9204	0·9232	0·9180	0·9264
Effect of cold (− 20°)	Slightly viscid	Slightly viscid	Opaque and viscid	Viscid and slightly opaque
Parts potash required to saponify 1000 of oil	181·4	189·1	183·0	194·4
Bromine absorbed by 100 of oil	70·0	77·0	53·74	90·5
Action of nitric acid	Coffee-brown colour	Dark-brown	Action slight	Dark-brown.
„ sulphuric acid	Light-brown to red-brown	Dark-brown	Yellow to orange	Dark-brown to purple.
Zinc chloride solution	Muddy-brown with purple shade	Purple-brown	No action	Muddy-brown.
Elaïdin test	Light yellow, hard	Citron-yellow, soft	White, hard	Not solidified.

The almond oil is inserted for comparison. D. A. L.

Analyses of Tumbeki. By E. J. Eastes and W. H. Ince (*Pharm. J. Trans.* [3], **16**, 682—683).—Tumbeki is the name given to the dried leaves of *Nicotiana persica*, extensively smoked in Persia. Shiraz tumbeki has the highest value. Estimation of nicotine:—The most trustworthy method for this purpose is to exhaust dry and powdered tumbeki with dilute sulphuric acid, neutralise the extract with soda, and separate the alkaloïd with chloroform, and subsequent treatment with dilute sulphuric acid. The acid solution of the alkaloïd is then treated with a standard solution of Mayer's reagent, until no more precipitate, ($C_{10}H_{16}N_2I_2,HgI_2$), is formed. For the determination of saccharine matter, dry tumbeki is exhausted with boiling water, the extract fermented with yeast, and the alcohol formed estimated. Basic lead acetate does not remove fermentable matter from the

aqueous infusion of tumbeki. Four varieties of tumbeki showed the following composition per cent. :—

Constituent.	Tumbeki from			
	Ispahan.	Hedjaz.	Kechan.	Shiraz.
Nicotine	5·4945	2·046	2·909	5·835
Saccharine matter	2·64	2·85	5·58	3·355
Matter soluble in water	42·0	42·3	39·9	55·6
Ash	22·0	28·5	28·5	26·15

In all cases, the ash contained :—Sodium, potassium, lithium, magnesium, calcium, iron, aluminium, silica, chlorine, phosphoric, sulphuric, and carbonic acids. D. A. L.

Experiments in Grafting between Plants of different Species. By Strassburger (*Bied. Centr.*, 1886, 248—249).—The experiments were made to ascertain the limits between which plants of distinct species could be grafted on each other, and also the influence of layering and inoculation.

Potato plants were layered down before the formation of tubers, they struck out strong rootlets, inoculated with *Datura stramonium* and *Physalis alkekengi* they grew rapidly; with tobacco inoculation the growth was slower but good, but much worse with deadly nightshade.

In other experiments the potato was inoculated on tobacco, &c., but unsuccessfully; the author attributes the failure to the late time of year in which the experiments were made. A Chilian plant of a different family, *Schizanthus grahami*, was also grafted with success.

In none of these cases was the influence of inoculation on the tubers of the potato very perceptible; in that by *Datura stramonium*, the tubers were exceptionally fine, but the blossoms fell off before formation of fruit, and perceptible traces of atropine were found. J. F.

Composition of Certain Fodder Plants. By M. Märcker (*Bied. Centr.*, 1886, 241—245).—*Vicia villosa*, or sandvetch, grows wild in North Germany, and yields satisfactory crops in soil of very inferior quality, dry, calcareous soils giving the best results. No analysis has hitherto been published, the author analysed the plant at three stages of its growth: the following are the figures for the fresh and the dried substance at the end of bloom, 29th July :—

	Fresh substances.	Dry.
Water	81·0 per cent.	—
Proteïn	3·91 „	20·58
„ containing pure albumin	3·44 „	18·10
Fat	0·69 „	3·65
Non-nitrogenous extract	6·18 „	32·51
Fibre	6·53 „	34·35
Ash	1·69 „	8·91

These figures indicate the sandvetch to be a valuable fodder material, superior to other vetches, of which the author gives analyses.

The beinwell, *Symphytum asperrimum*, is a plant introduced from the Caucasus; it is very hardy and prolific, propagated by layers, but without agreeable flavour, and not much relished by cattle. It is recommended for ensilage with other fodder plants, when it would be eaten readily. Analysis shows a very large proportion of ash, pointing to considerable exhaustion of the soil. J. F.

Composition and Relative Digestibility of Feeding-stuffs. By E. F. Ladd (*Amer. Chem. J.*, **8**, 47—51).—The feeding-stuffs—hay and coarse fodders, bye-products such as linseed and cotton-seed meal, bran, &c., and grains—were analysed and then digested with pepsine in presence of dilute hydrochloric acid; the undigested portion being determined and examined. Bean, linseed and pea-meals are most digestible, and badly cured hay least; cotton-seed meal is also very digestible, and is moreover very rich in albuminoïds, &c. H. B.

German and American Clover. By Troschke (*Bied. Centr.*, 1886, 266).—America has recently exported large quantities of clover-seed to Germany. The native growers assert that the hay produced from it possesses less nutritive properties than that from native seed. The author analysed samples of American and three other kinds; he found their composition as nearly identical as possible; all had about the same fodder value. J. F.

Chili Saltpetre or Ammonium Sulphate. By M. Märcker (*Bied. Centr.*, 1886, 233—237).—The author has already studied the relative manurial values of these two substances (see Abstr., 1885, 1156). That the nitrogen in the ammonium salt is less effective than that in the sodium nitrate, weight for weight, has been proved by many experiments, but the low price of the ammonium sulphate has induced the author to further investigate the subject. At present prices, in Germany, 20 to 20·5 lbs. of nitrogen in ammonium sulphate cost but the same amount as 15·5 lbs. in sodium nitrate.

Experiments were made with wheat, barley, sugar-beets, and potatoes, both the manures being applied in autumn and being in every way treated alike.

The author comes to the conclusion that whilst the present difference in price exists, it would pay the farmer to use the ammonium salt and other ammoniacal manures.

In the course of the experiments, the author found that the ammoniacal salt gave very unsatisfactory results when used with farmyard manure. J. F.

Failure of Ammonium Sulphate as a Manure. By T. Brown (*Chem. News*, **53**, 182).—In experiments with ammonium sulphate as a manure, the author has obtained results sometimes superior, sometimes equal, and sometimes much inferior to those obtained in comparative experiments with sodium nitrate. In some special experiments, it was noted that when ammonium sulphate was

mixed with a light calcareous soil (containing over 17 per cent. calcium carbonate and over 72 per cent. silica), abundant evolution of ammonia ensued and continued for several days. This evolution of ammonia can be checked by covering the mixture with about an inch of fresh soil. These results explain to a certain extent some facts suggested by the experiments referred to above: as for example, the failure of ammonium sulphate when applied either to soils containing over 10 per cent. calcium carbonate or as a top dressing, as compared with satisfactory results attending its application to loams, clays, or to crops permitting of its being harrowed or ploughed in.

D. A. L.

Manner of Applying Artificial Manures. By I. VAN DEN BERGHE (*Bied. Centr.*, 1886, 240—241).—The experiments noted in this paper were made to ascertain whether the use of artificial manures as top dressing or ploughed in would yield the better result. The soil was a light sand containing but 3·70 per cent. of clay with an absorptive capacity of 31·90 per cent. The manures were of three kinds, and the crop potatoes. The manures were applied to the surface of one set of plots, in the other set they were dug in to a depth of 22 cm. With all three manures, the parcels in which they were dug in yielded considerably larger crops than the top-dressed parcels, and the potatoes were also richer in starch. J. F.

Lime Waste from Sugar Factories. By HOLDEFLEISS and STROHMER (*Bied. Centr.*, 1886, 277—279).—The authors have investigated this substance with regard to its value as a manure. Of 11 samples, the moisture varied from 38 to 72 per cent.; in the dry substance, there was found nitrogen, 0·24 to 0·44; phosphoric acid, 0·011 to 2·15; potash, 0·14 to 0·94; lime, 33·4 to 57·6 per cent. The value as manure is therefore small; it is recommended as a component of compost heaps; on heavy acid or non-calcareous soils it may be of utility. J. F.

Analytical Chemistry.

New Apparatus for Gas Analysis. By E. H. KEISER (*Amer. Chem. J.*, **8**, 9—16).—The volume of gas used for analysis and left after the action of absorbents is determined by the weight of the mercury it displaces. The use of long calibrated tubes is thus avoided and the accuracy of the measurements at the same time increased. H. B.

Quantitative Evaporation of Liquids in the Spheroïdal State. By E. BOHLIG (*Zeit. anal. Chem.*, **25**, 187—190).—Liquids, such as natural waters, of which it is required to determine the total residue, can very easily be evaporated in the spheroïdal state. The measured liquid (50 c.c.) is slowly dropped into a platinum basin

maintained at a red heat, where it evaporates in the well known manner. The residue is obtained as a spherical globule lying loose in the basin, and from the small extent of its surface can be weighed in an open vessel without appreciable absorption of moisture. Since the liquid does not come in contact with the evaporating basin the latter is not attacked under any circumstances. Alkalis, however, and many salts are liable to decrepitate when carried to complete dryness. In these cases, or in the presence of substances which will not bear a higher temperature than 70° or 80°, the liquid globule can finally be poured from the still red-hot basin into a vessel in which the evaporation is to be finished. M. J. S.

Direct Determination of Chlorine in presence of Bromine. By G. Vortmann (*Zeit. anal. Chem.*, **25**, 172—179).—In reply to the criticisms of Berglund (Abstr., 1885, 836) on the author's method (*ibid.*, 1882, 1230), it is shown by numerous test analyses that, when the amount of the bromide does not exceed that of the chloride, fairly good results can be obtained under widely varied conditions of treatment. The expulsion of the bromine by heat is, however, attended with the formation of a small quantity of bromate, and the author, therefore, adopts Berglund's suggestion to expel the bromine by a stream of air in the cold. In this case, a 5 per cent. acetic acid should be used; a stronger acid favours the formation of bromate. Four or five hours are required for the complete removal of the bromine. M. J. S.

Photochemical Reaction of Schutzenberger's Oxymetric Solution. By V. Jodin (*Compt. rend.*, **102**, 767—768).—Schutzenberger's reagent for oxygen (Coupier's blue decolorised by a hyposulphite) becomes blue when exposed to light, even when out of contact with oxygen. If the liquid is kept in the dark, it undergoes no change, even when the temperature is maintained at 50°. This reaction must be taken into account in using this reagent to detect the presence of oxygen (see Regnard, this vol., p. 254). C. H. B.

Nitrogen Determination by Kjeldahl's Method. By A. Rindell and F. Hannin (*Zeit. anal. Chem.*, **25**, 155—156).—The short tube of beads employed by Pfeiffer and Lehmann (Abstr., 1885, 179) does not entirely arrest caustic alkali. This is due to the condensation of water on the beads and the subsequent spirting of this into the condenser. By enclosing the bead tube (8 cm. long by 12 mm. diameter) in a wider tube kept full of steam, the condensation is prevented and every trace of alkali is stopped.

Litmus solutions do not all possess the requisite sensitiveness. The treatment with lime recommended by Schlösing (Grandeau's *Handbuch f. agricult. Anal.*, 154) affords an excellent indicator. M. J. S.

Detection of Minute Traces of Nitric Acid. By Curtman (*Zeit. anal. Chem.*, **25**, 225).—A solution of pyrogallol is added and then 10 to 12 drops of concentrated sulphuric acid so as to form two layers in the test-tube. The presence of nitric acid is indicated by a

brown colour—or yellow if the quantity is smaller—where the two layers meet. A tenth of a milligram of nitric acid in a litre of water can be detected with certainty. M. J. S.

Determination of Arsenic and Boric Acids in Mineral Waters. By R. Fresenius (*Zeit. anal. Chem.*, **25**, 202—205).—In a recent analysis of the water of the Kochbrunnen at Wiesbaden the above constituents were determined as follows:—

Arsenic acid.—The iron present was peroxidised by sodium hypochlorite and hydrochloric acid. Ferric chloride and then an excess of precipitated calcium carbonate were added. The precipitate was repeatedly distilled with ferric chloride and hydrochloric acid, and the arsenic was precipitated from the distillate by hydrogen sulphide. From 92·65 litres of water, 0·015 gram of As_2S_3 was obtained.

Boric acid.—The water, rendered alkaline by potassium carbonate, was strongly concentrated. Since the precipitate which separated contained some boric acid, it was dissolved in hydrochloric acid and reprecipitated by potassium carbonate. The two filtrates were evaporated nearly to dryness, then acidified, and the boric acid was extracted by alcohol. After adding potash, the alcohol was distilled off; the residue was again acidified and extracted with alcohol, and this treatment was repeated a third time. The saline mass was then treated with hot water and the solution was filtered from a residue of magnesium hydroxide, which, as it was not free from boric acid, was redissolved and reprecipitated. The boric acid was now thrown down by Stromeyer's process as potassium borofluoride, which was subsequently freed from silicofluoride by eight evaporations with ammonia. From 36·35 litres of water, there was obtained 0·0756 gram of potassium borofluoride. M. J. S.

Estimation of Silicon in Organic Compounds. By A. Polis (*Ber.*, **19**, 1024—1027).—The methods previously employed give very unsatisfactory results, but the following method, founded on that of Kjeldahl for the determination of nitrogen, seems to be quite accurate.

The substance is dissolved with the aid of heat in about 20 c.c. of sulphuric acid mixed with fuming sulphuric acid, and a few c.c. of concentrated potassium permanganate solution is cautiously dropped in from a burette, the mixture then being heated until it is decolorised. The addition of permanganate and heating is repeated until the substance is completely decomposed. The liquid after cooling is diluted with water and the silicic acid collected and ignited, gently warmed with hydrochloric acid to remove the manganoso-manganic oxide which is invariably carried down with it, washed, again ignited and weighed. If, however, as sometimes happens, the silica is still contaminated with manganese, it must be fused with sodium carbonate and potassium nitrate, and the silica in the fused mass estimated as usual. A. J. G.

Organic Elementary Analysis. By P. Jannasch and V. Meyer (*Ber.*, **19**, 949—950).—This paper is a preliminary notice of a method

of combustion analysis in which the carbon, hydrogen, and nitrogen can be simultaneously determined. The combustion is effected in an atmosphere of pure oxygen, the excess of which is absorbed by chromous chloride. The operation is stated to be nearly as simple as the ordinary carbon and hydrogen combustion. No details are given.

Titration of Soda in Presence of Aluminium, Vanadium, and Tungsten. By E. B. (*Zeit. anal. Chem.*, **25**, 186—187).—When methyl-orange is used as indicator, the whole of the soda in combination with alumina appears in the result as alkali. Soda containing vanadium or tungsten, when just supersaturated with acid, gives a brown colour, the red only appearing with a considerable excess of acid. In such cases, litmus-paper must be used. M. J. S.

Separation and Estimation of Copper, Cadmium, and Zinc; of Nickel and Cobalt; and of Manganese and Iron. By A. Carnot (*Comp. rend.*, **102**, 678—681).—The separation of copper, cadmium, and zinc by means of ammonium or sodium thiosulphate has already been described (this vol., p. 580). After the removal of the copper and cadmium, the zinc can be precipitated alone from a solution which also contains nickel, cobalt, iron, &c., by adding a slight excess of ammonia, then acidifying slightly with oxalic acid, and passing a rapid current of hydrogen sulphide through the cold and dilute solution.

If the filtrate from the zinc contains nickel, cobalt, or iron alone or nickel and iron together, they can be precipitated in the usual way. If nickel, iron, and manganese are present, the filtrate is neutralised with ammonia, mixed with an excess of sodium or ammonium acetate, slightly acidified with acetic acid, and a current of hydrogen sulphide is passed through the liquid for some time. Iron and nickel are precipitated, and the manganese in the filtrate can be precipitated with ammonium sulphide. This method of separating iron and manganese is preferable to the ordinary basic acetate method when the amount of iron is considerable.

A similar method may be used with advantage to separate iron and zinc. The solution is almost exactly neutralised with ammonia, diluted, mixed with ammonium chloride and a very small quantity of ammonium oxalate, and the zinc precipitated by a current of hydrogen sulphide. C. H. B.

Electrolytic Estimation of Mercury. By L. de la Escosura (*J. Pharm.* [5], **13**, 411—413).—The following processes are exclusively employed at the Almaden mines.

I. The mineral is boiled with hydrochloric acid and potassium chlorate; after the decomposition is complete, and all odour of chlorine has disappeared, 20 to 30 c.c. of a saturated solution of ammonium sulphite is added, the mixture boiled for a few minutes, and allowed to settle. The sulphite precipitates selenium and tellurium. After filtering, the solution amounting to 200 c.c. is submitted to electrolysis in a glass vessel, one electrode being platinum and the other gold. With two Bunsen's elements the whole of the mercury

is precipitated in 24—30 hours. The increase in weight of the negative gold electrode gives the amount of mercury.

II. The mineral is attacked in a platinum capsule with a mixture of water, hydrochloric acid, and ammonium sulphite; for a mineral containing 10 per cent. of mercury, 0·2 gram would be taken together with 10 c.c. of hydrochloric acid, 90 c.c. of water, and 20 c.c. of sulphite. The capsule, 9 cm. in diameter, receives a disc of gold 4 cm. in diameter joined to the zinc pole of the battery; the capsule is connected with the other pole. In 24 hours the mercury is completely deposited. This method, after a year's experience, has been found more satisfactory than any other method either wet or dry.

J. T.

Determination of Alumina by Titration. By K. J. Bayer (*Zeit. anal. Chem.*, **25**, 180—183).—For determining the excess of soda in the author's process (p. 281), it is necessary to boil vigorously and maintain the alkaline reaction of the liquid until one or two drops of acid suffice to produce the change of colour. The solution must not contain more than 0·1 per cent. of alumina. If an excess of acid has been added, it cannot be titrated back with soda, since basic aluminium sulphates are then formed. Phenolphthaleïn is far more convenient than litmus as the indicator.

The soda in aluminates can also be titrated after removal of the alumina by carbonic anhydride, but it is necessary to pass the gas in slowly, and to keep the dilute solution freely boiling and constantly shaken, otherwise the alumina will carry down soda.

M. J. S.

Determination of Alumina in Aluminates. By E. B. (*Zeit. anal. Chem.*, **25**, 183—186).—The author had used, but not published, a process identical with Bayer's (see above) three years earlier. The tropæolin OO is to be used, not that known as OOO, but dimethyl-orange is preferable. The titration of the excess of alkali is so troublesome and uncertain, even when using phenolphthaleïn, that it is easier to determine it by distilling with ammonium chloride, and collecting the ammonia in standard acid. This can then be titrated with standard sodium carbonate, using methyl orange as indicator. A little rosolic acid added to the distillation flask shows, by becoming yellow, the moment when all the ammonia is expelled.

M. J. S.

Qualitative Separation of Gold and Platinum from Tin, Antimony, and Arsenic. By R. Fresenius (*Zeit. anal. Chem.*, **25**, 200—202).—Instead of the somewhat inconvenient method of heating the sulphides in a stream of chlorine, they may be intimately mixed with about 5 parts of ammonium chloride and 1 part of ammonium nitrate, and heated in a porcelain boat, over which a current of air is aspirated into water. The gold and platinum are left in the metallic state in the boat. The other metals are found as chlorides in the sublimate and in the water.

M. J. S.

A New Thickening Material for Mineral Lubricating Oils. By L. Marquardt (*Zeit. anal. Chem.*, **25**, 159—160).—The substance

sent into commerce for this purpose as "liquid gelatine" is a 10 per cent. solution of an aluminium soap in petroleum. It is a nearly clear, brown, syrupy, stringy, tenacious liquid, with a tendency to gelatinise. It is intended for addition to the lubricating oil, but its use cannot be recommended, since on addition of water the aluminium soap separates and produces a glutinous emulsion. It also froths when warmed. The presence of this soap in a lubricating oil can be detected by determining the ash, which in a pure oil does not exceed 0·058 per cent. Or its amount may be ascertained by digesting the oil with dilute hydrochloric acid, removing the fatty acid by a caustic alkali, and weighing the residual petroleum.

M. J. S.

Determination of Nitrogen in Wine Must and Lees. By P. Kulisch (*Zeit. anal. Chem.*, **25**, 149—154).—In the above substances, Kjeldahl's method (Abstr., 1884, 364) as described by Balcke (*Wochenschr. f. Brauerei*, **1**, No. 11) and Morgen (*Chem. Zeit.*, **7**, No. 25) does not give concordant results. With the following precautions, however, the results obtained agreed perfectly amongst themselves. The acid used consists of equal volumes of concentrated and of fuming sulphuric acid, and contains 100 grams of phosphoric anhydride per litre. Blank experiments are necessary in order to correct for ammonia in the reagents. It is essential that, before adding the permanganate, the heating should be continued until the solution becomes perfectly colourless. The time required for this can be much shortened by the addition of a little mercury. The permanganate cannot safely be dispensed with, although good results have sometimes been obtained without it. The arrangement advocated by Pfeiffer and Lehmann (Abstr., 1880, 179) to prevent alkali from being carried over (comp. p. 648) during the distillation, is unnecessary if the quantity of soda added is such as to produce only a slow evolution of hydrogen, and the mixture is distilled from a long-necked flask placed obliquely. As the quantity of sugar in must renders the treatment with sulphuric acid very troublesome, it should, when possible, be removed by fermentation before evaporating to dryness. The fermentation, however, requires ten days. It causes no loss of nitrogen.

M. J. S.

Does every Wine contain Tartar? By M. Petrowitsch (*Zeit. anal. Chem.*, **25**, 198—200).—It is asserted by Dietzsch that a wine which deposits no tartar during 24 hours after admixture with ether alcohol is undoubtedly artificial. The author has, however, examined a Carlowitz wine of unquestionable genuineness which did not give a trace of tartar when thus treated. The specimen was a wine of the first pressing (Ausbruchwein) six years old. It contained 14·65 volumes per cent. of alcohol, and its total acidity was equal to 0·82 per cent. of tartaric acid. The low temperature of the Carlowitz cave cellars may have favoured the separation of the tartar. It follows that whilst the absence of tartar from wines which contain little alcohol would be strong evidence of their not being genuine, this criterion does not necessarily apply to wines of higher alcoholic strength.

M. J. S.

General and Physical Chemistry.

Velocity of Light in Quartz. By K. Exner (*Jahrb. f. Min.* 1886, i, Ref., 388).—If v_1 and v_2 represent the velocities of two plane waves propagated in the same direction in quartz, and v'_1 and v'_2 the velocities of two plane waves propagated in the same direction in a crystal which does not possess the power of optical rotation, but which in directions perpendicular to the optic axis has the same velocity of light as quartz, then it follows from the theories of Cauchy and V. v. Lang that—

$$\tfrac{1}{2}(v_1 + v_2) = \tfrac{1}{2}(v'_1 + v'_2),$$

that is to say, for any direction of propagation in quartz, the arithmetical mean of the two velocities of propagation is equal to the arithmetical mean of the velocities which would correspond with the same direction of propagation in a crystal without the power of optical rotation, but with the same refraction. From this may be deduced Cornu's law that in the direction of the optic axis of quartz, the arithmetical mean of the two velocities of propagation of light is equal to the velocity of propagation of the ordinary wave in directions perpendicular to the optic axis. B. H. B.

New Apparatus for Electro-chemical Investigations. By N. v. Klobukoff (*J. pr. Chem.* [2], **33**, 473—479).—A "universal support" for electrolysis is described with sketch, and also an apparatus for the examination of liquid electrolytes which require an estimation of the gases evolved from them, and for liquids which are unstable in presence of air. N. H. M.

Electrical Conductivity of Aqueous Solutions of Potassium Chloride. By E. Bouty (*Compt. rend.*, **102**, 1097—1100).—The specific resistance of a normal aqueous solution of potassium chloride, containing 74·59 grams per litre, is 15·415 ohms. Between 0° and 30°, the resistance can be expressed with sufficient accuracy by the formula $r_t = \frac{r_0}{1 + \alpha t}$, in which r_0 is the specific resistance. The following table gives the absolute values of the specific resistance r_0, the relative values of the molecular resistance ρ_0 referred to that of a normal solution, and the values of α.

No. of equivalents.	r_0.	ρ_0.	α.
3	5·172	1·007	0·0230
2	7·785	1·010	0·0259
1	15·415	1·000	0·0291
0·5	30·49	0·989	0·0302
0·2	72·23	0·937	0·0326
0·1	141·00	0·915	0·0327
0·01	1325·00	0·860	0·0333
0·001	12697·00	0·824	0·0333

Between 3 and 0·5 equivalents, the molecular conductivity ρ_0 is almost constant whilst the value of α increases rapidly, but in dilute solutions the value of α remains sensibly constant whilst the molecular conductivity decreases considerably, and tends to a limit not very far removed from 0·75, but the determination of the exact value is rendered difficult by the variations in the composition of the distilled water. C. H. B.

Electrical Conductivity of Supersaturated Salt Solutions. By C. Heim (*Ann. Phys. Chem.* [2], **27**, 643—656).—This paper contains an account of experiments on the electrical conductivity of various soluble metallic sulphates, chlorides, and carbonates made to determine whether any change of conductivity is manifest at their point of saturation, which would indicate an alteration of equilibrium of salt and water molecules respectively. But in all cases examined, the curves of the resistance in terms of temperature varying from 60° to 10° were perfectly continuous, and showed no inflection at the point at which the solution became supersaturated. In fact the curve of conductivity was continuous even to the point at which the solution became suddenly solid throughout, when there was a sudden decrease of conductivity. In general, the results were in accordance with Kohlrausch's formula $K_t = K_0(1 + \alpha t + \beta t^2)$, deduced from experiments with unsaturated solutions, provided that the solutions remained perfectly liquid; but directly individual crystals separated, this formula is no longer valid, as the conductivity decreases more quickly than required by the formula, the change becoming greater the more speedily the solution is cooled below its saturation point. V. H. V.

Secondary Electrolysis. By E. Semmola (*Compt. rend.*, **102**, 1059—1060).—If a small ribbon of platinum is immersed in a voltameter containing acidulated water, in such a way that its ends are opposite the electrodes of the voltameter, and a powerful current is passed through the latter, hydrogen and oxygen are evolved not only from the electrodes but also from the ribbon. This secondary electrolysis varies greatly with different conditions, and ceases altogether when the current is not strong, but if oxidisable metals are used instead of platinum it becomes much more energetic. The phenomena are well seen with amalgamated zinc, which is not attacked by acidulated water except when the current passes. When the circuit containing the voltameter is closed, hydrogen is given off from one half only (the negative half) of the zinc, whilst oxygen is absorbed by the other half. If several pieces of zinc are immersed in the water in the voltameter, hydrogen is given off from each of them. This secondary electrolysis is due to a current derived from the immersed zinc. C. H. B.

Magnetism of Magnetite. By F. F. Hornstein (*Jahrb. f. Min.*, 1886, i, Mem., 253—254).—Kenngott (*Jahrb. f. Min.*, 1885, **1**, 240) observed polar magnetism in unaltered magnetite. Observations on octahedra of magnetite from Zermatt have induced the author to

conclude that crystals of magnetite and unaltered massive magnetic fragments behave exactly like soft iron, inasmuch as they become momentarily influenced by terrestrial magnetism and become polar magnetic. The polar magnetism observed by Kenngott is perhaps identical with that produced by induction. B. H. B.

Specific Heat of Antimony and its Compounds. By L. Pebal and H. Jahn (*Ann. Phys. Chem.* [2], **27**, 584—605).—In this paper, results are given of determinations of the specific heats of metallic antimony in the ordinary and explosive forms, as also of its chloride and bromide at temperatures varying from + 33° to − 80°, the latter point, or more exactly − 79·35°, being an independent determination of the temperature produced by the evaporation of solid carbonic anhydride under an atmospheric pressure of 743 mm. The specific heat of the metal, whether determined directly or deduced from that of its compounds, increases with decrease of temperature. This point is exemplified by the following results :—

Atomic Heat of Metal (Sb = 121).

Temperature.	Direct determination.	Explosive condition.	Deduced from chloride.
Between + 33° and 0°	5·99	6·72	6·34
„ 0 „ − 21	5·88	6·24	5·62
„ − 20 „ − 75	5·72	6·52	5·67

The atomic heat capacity of antimony is not altered by the change from its combination with its halogen-derivative in the explosive condition into the metallic state. The calorimetric measurements were made with a Bunsen's ice calorimeter, the weight thermometer method being used; the lower temperatures were independently ascertained by a thermopile and galvanometer, and the lowest by means of an air thermometer corrected by an independent observation of the coefficient of expansion of gas. V. H. V.

Heat Equivalent of Hydroxybenzenes. By F. Stohmann, P. Rodatz, and H. Herzberg (*J. pr. Chem.* [2], **33**, 464—470; compare Abstr., 1885, 857).—The heat of combustion of phenol (burnt in a lamp) is 7716 cal. (or 725304 cal. per gram-molecule), the number previously found by burning phenol with potassium chlorate was 7681 cal. Favre and Silbermann (*Ann. Chim. Phys.* [5], 31, 443) give the number 7842 cal., but probably used less pure phenol. The results obtained with pyrocatechol and resorcinol (6075 and 6098 cal. respectively) confirm those previously published. The heat of combustion of quinol is 6092 cal.; the three isomerides have therefore nearly the same heat of combustion; the variations are, however, in the same direction as those in the heat of neutralisation as given by Berthelot and Werner (Abstr., 1885, 628). The heat of combustion of pyrogallol and of phloroglucinol is 616266 and 617652 cal. per gram-molecule respectively; the heat of neutralisation of the two compounds is 13803 and 18269 cal. (Berthelot and Werner, *loc. cit.*). N. H. M.

Heat Equivalent of the Hydroxyl-groups in the Hydroxybenzenes. By F. Stohmann (*J. pr. Chem.* [2], **33**, 470—472).—In comparing the heat of combustion of benzene and its hydroxy-derivatives (compare preceding Abstract) with the heat of formation, it is found that the substitution of each hydroxyl-group for hydrogen in benzene raises the heat of formation by an average of 53·6 Cal.

The same holds good in the case of hydroxy-derivatives containing other radicles; thus the heat of formation of benzoic acid is 766282 cal., that of salicylic acid 712356 cal.

On the other hand, the substitution of two hydroxyl-groups in succinic acid causes a rise of 2 × 47·2 Cal. in the heat of formation, whilst the heat of formation of glycerol is only 2 × 40·5 Cal. higher than that of isopropyl alcohol. Hence it would appear that the increase caused by the presence of hydroxyl varies according to whether it replaces hydrogen in CH, CH_2, or CH_3, and that the increase amounts in each case to 53·6, 47·2, and 40·5 Cal. respectively.

N. H. M.

So-called Critical Pressure of Solid Substances. By V. v. Richter (*Ber.*, **19**, 1057—1060).—Critical pressure was defined by Carnelley as the pressure "below which no amount of heat can melt the substance," and by Petterson as that "at which the boiling point of the liquid substance coincides with the melting point of the substance in the solid state" (comp. L. Meyer, Petterson, Haas, Carnelley, Abstr., 1881, 133). The following definition shows more clearly the conditions and causes of the phenomenon of non-melting: A liquid can only exist as such when the pressure on it is greater than the tension of the vapour at the given temperature; when the pressure is smaller the substance exists only as a gas. If a fusible substance is under a lower pressure than that which corresponds with the tension of the vapour at the temperature of the melting point, it cannot melt when heated, but passes at once to the gaseous state.

The usual explanation of the fact that liquid carbonic anhydride solidifies as it issues from the vessel in which it is contained, is that the solidification is caused by abstraction of heat by the quick evaporation of the liquid; the true reason being decrease of pressure below the melting point tension.

The non-melting of benzene below the pressure of 35·6 mm. can be readily shown in the following way: A few c.c. of benzene are put into a short tube provided with a side tube, and the tube closed by a cork through which a thermometer is passed; the side tube is connected with a vacuum reservoir and a pump. The benzene is then solidified by means of ice, and the pressure in the tube reduced to below 35·6 mm. So long as the pressure does not rise above 35·6 mm. the benzene in the tube cannot be melted however much the tube is heated.

The reason why a solid substance at a low pressure cannot be heated above its melting point is that there is a definite vapour-tension corresponding with each temperature, and, inversely, a definite temperature corresponds with a given pressure, above which the compound cannot be heated. Thus, in the case of mercuric chloride, with

a melting point tension of 420 mm., the following corresponding pressures and temperatures were found: at 20 mm., 200°; at 130 mm., 240°; at 250 mm., 265°; at 370 mm., 270°. These numbers are only approximate, and are intended to show that a definite pressure exists for every temperature. N. H. M.

Dissociation of Nitrogen Peroxide. By E. and L. Natanson (*Ann. Phys. Chem.* [2], **27**, 606—623).—In this paper, determinations are given of the density of nitrogen peroxide at temperatures varying from — 12° to 151°, and pressures varying from 20 to 760 mm. A modification of Regnault's twin glass globes method was used, the pressure of the gas within the globe being determined by a manometer. The method of ascertaining exactly the cubic capacity of the globe, the pressures recorded by the manometer, and the temperatures at which observations were made, as also the general procedure, are described in detail.

The general formula for such cases of dissociation is, according to Gibbs, Boltzmann, and van der Waals, $p = A\frac{d-\delta}{(2\delta-\delta)^2}$, in which p is the pressure, d the density observed, and δ, 2δ, the theoretical limit of density corresponding in this particular case with the molecule N_2O_4 and NO_2, whilst $A = f(t)$ is a function of the temperature. But different observers vary as to the exact nature of the function, for, according to Gibbs and van der Waals, $A = Me^{-\frac{a}{b}}$, but, according to Boltzmann, $A = Me^{-\frac{a}{b}t}$. If curves be drawn representing density in terms of pressure, the temperature being constant, these isothermals, as it is convenient to designate them, give values for A which are not concordant with those indicated by the formula of Gibbs and Boltzmann. The observations herein detailed show that these isothermals incline with increase of temperature more nearly to the axis of the abscissæ, and at the same time become more flattened out, or, expressed in words, the higher the temperature, the smaller the effect of pressure on the degree of dissociation.

As then the isothermals approach the axis of d, when the densities δ and d converge, so for every such isothermal there is a point where the pressure for a given value of e is at the maximum P, the nature of which is as follows: if a gas be submitted to pressure permanently greater than or equal to P, then the gas can be completely dissociated, namely, can pass from the limit δ to d without passing through a state of aggregation, in which it differs from Boyle's law to a greater degree than is required for the corresponding value of e. From these considerations, it appears that the best form of the equation is $p = \frac{1}{e}\frac{(2d-\delta)(d-\delta)}{d}$: the values calculated from it are concordant with those observed. V. H. V.

The Inner Friction Constants, and the Specific Viscosity of Organic Liquids and their Aqueous Solutions. By J. Traube (*Ber.*, **19**, 871—892).—The results of numerous experiments made with different organic liquids, point to the following conclusions:

the curves showing the concentration and specific weights coincide very nearly for alcohols, whilst in the case of acids of the same degree of concentration, the specific weights increase as the molecular weight of the acid decreases. The specific weights of formic acid solutions increase with concentration, whilst solutions of propionic and butyric acids show a maximum of density for a certain medium degree of concentration.

Graham and others have already shown that the friction constants of the acids, as such, decrease from formic to propionic acid, but again increase from propionic to the higher acids. The curves constructed from the concentration and friction constants (for all temperatures) for formic, acetic, and propionic acid, intersect each other; whilst the curve for butyric acid only intersects the formic acid curve. It is probable that the acid curves are normal for higher temperatures.

The formic acid curve (as also in the case of specific weights) is the only one which rises in a nearly straight line. Isobutyric acid has less viscosity than normal butyric acid, but in solution it has a greater viscosity.

At a temperature of about 20°, the maximum of viscosity corresponds more or less completely with the maximum of contraction; but at higher temperatures a shifting of the maximum of viscosity takes place.

The paper concludes with further theoretical remarks on these results. It is probable that the constant η contains a factor which is independent of the adhesion of the liquid to the walls of the vessel, and varies with the temperature (comp. Abstr., 1885, 1033).

N. H. M.

Rate of Chemical Change between Iodic and Sulphurous Acids. By H. Landoldt (*Ber.*, **19**, 1317—1365).—Iodine is instantaneously liberated on mixing concentrated solutions of iodic and sulphurous acids, but with dilute solutions this change occurs after an appreciable interval of time, dependent on the ratio of the masses of the reacting substances, the degree of concentration, and the temperature. The variation of the rate of change as a function of the two former conditions is the subject of the present memoir. The reactions between iodic and sulphurous acids may be considered to take place in three stages: (I), sulphuric and hydriodic acids are formed thus: $3SO_2 + HIO_3 = 3SO_3 + HI$; (II), the hydriodic acid thus produced reacts with the iodic acid to yield iodine and water, thus: $5HI + HIO_3 = 3H_2O + 3I_2$; but (III), the iodine in equation II oxidises the sulphurous acid, thus: $I_2 + SO_2 + 2H_2O = H_2SO_4 + 2HI$. These changes are repeated until all the sulphurous acid is oxidised; not until then does the iodine reveal its presence by the starch reaction.

By independent experiments, it is shown that reaction (III) is unaltered by change of concentration, and is practically instantaneous, and that (II) continues to be instantaneous for all concentrations within the limits of the experiments herein detailed, although with very dilute solutions the time required is appreciable.

The method of procedure consisted in mixing the solutions of sulphurous and iodic acids as rapidly as possible, and observing the

time required for the production of the blue colour of the iodine starch reaction. This process was found preferable to a determination of the hydriodic and sulphuric acids after a known interval of time. The sources of error, such as heterogeneity of the mixture, oxidation of the sulphurous acid by inevitable contact with the atmosphere, time consumed in the process of mixture, and the personal equation of the time record, are discussed in full.

Two series of experiments were made at a constant temperature of 20°: *firstly*, those in which the ratio of sulphurous acid and water was kept constant; and, *secondly*, those in which the ratio of sulphurous and iodic acids was constant, whilst that of the water was varied. The experimental results are given in a series of tables.

Discussion of the Results.—Let t, t_1, &c., be the intervals of time observed, which elapsed between the completion of the mixture and the iodine starch reaction, and let C_S and C_I represent the concentration of the sulphurous and of the hydriodic acids respectively. Then in the first set of experiments $\frac{C_I}{C_{I'}} = p$ and $\frac{t}{t_1} = q$, equations which may be put in the form $f(C_I) = qf(pC_I) = 0$; if then $f(C_I)$ be taken as equal to $C_I{}^{-y}$, then $y = \frac{\log p}{\log q} = \frac{\log t - \log t_1}{\log C_{I'} - \log C_I}$, in which y is an index between 1 and 2. By combining different sets of experiments, different values were obtained for y, the mean of which gives finally the values for the constant k in the general expression for all cases, $t = \frac{k}{C_I{}^y}$, which expresses the time required for the oxidation of a given quantity of sulphurous acid as a function of the concentration of the iodic acid. The mean value for y obtained was 1·642. On comparing the observed with the calculated results, the values were found to be concordant within a small fraction of a second.

Similarly for variations of concentrations of sulpurous and iodic acids, as in the second series of experiments, $y = \frac{\log t - \log t_1}{\log C'_S.C'_I - \log C_S C_I}$, or $t = \frac{k_{,}}{(C_S C_I)^3}$, which can put on the form $t = \frac{K}{(C_S)^x (C_I)^y}$, where $K = k(C_S)^x x$, in which x is determined to be 0·904. The calculated and observed results in the second series are also compared, and found to be equally concordant with those above.

Discussion of the Meaning of the Indices x and y.—According to the researches of Guldberg and Waage were the reaction $3SO_2 + HIO_3 = 3SO_3 + HI$ reversible, when equilibrium is established $\frac{C_{3SO_3}\, C_{HI}}{C_{3SO_2}\, C_{HIO_3}} = \text{const.}$ (compare also Esson, *Phil. Trans.*, 1884, 683). In the case of dilute solution, van't Hoff ("L'Équilibre chemique dans les systèmes gazeux ou dissous à l'état dilué," *Arch. Néerlandaises*, **20**), the condition of equilibrium is $\frac{C^{3SO_3 i SO_3}\, C^{HI i HI}}{C^{3SO_2 i SO_2}\, C^{HIO_3 i HIO_3}} = \text{const.}$, in which i is a constant dependent on the diminution of the vapour-tension of

water by the substances dissolved, the osmotic pressure of the solution, and the lowering of the freezing point by the substances dissolved. The question is then discussed whether the value for the exponents $x = 0{\cdot}904$ and $y = 1{\cdot}642$ stand in a simple relation with the constant i of van't Hoff's formula. The values deduced for x and y from independent experiments on the lowering of the freezing point, &c., of the solutions used, agree with those found in the above research. But as Equation I is written above, namely, $3SO_2 + HIO_3 = 3SO_3 + HI$, it is *a priori* to be expected that $x = 3iSO_2$ and $y = iHIO_3$, not $x = iSO_2$ and $y = iHIO_3$, as shown by experiment. Thus then the equation, as written, does not represent the actual chemical change, but rather that one molecule of each reacting substance takes part in the change. It is probable that many other reactions which in the present methods of symbolism are represented as occurring between several molecules of the reacting substances, in reality are bimolecular; according to the experiments of van't Hoff, the decomposition of the hydrides of phosphorus and arsenic afford a case in point. Of such changes, van't Hoff remarks that the greater number of chemical equations merely express the quantitative relations between the reacting substances, but give a false representation of the mechanism of the change. V. H. V.

Lecture Experiment showing the Composition by Volume of Nitrous and Nitric Oxides. By E. H. Keiser (*Amer. Chem. J.*, **8**, 92—94).—Measured quantities of the gases are passed from a Hempel's gas burette through a tube containing heated metallic copper into a gas pipette; the nitrogen set free is drawn back into the burette, and its volume compared with the original volume. The tube containing the copper is 3 mm. internal diameter, and 10—12 cm. long; the copper is obtained by reduction of the oxide, and completely fills the tube, being kept in place by asbestos plugs.

H. B.

Inorganic Chemistry.

Preparation of Hydrogen and of Carbonic Oxide by Aid of Zinc-dust. By H. Schwarz (*Ber.*, **19**, 1140—1141).—Referring to G. Williams' observations (this vol., pp. 15 and 204), the author points out that a very convenient method for obtaining pure hydrogen and carbonic oxide is to mix 20 grams of zinc-dust with 22·8 grams of calcium hydroxide, or 30 grams of calcium carbonate respectively, and heat the mixture in a combustion tube. L. T. T.

Constitution of Hydrogen Peroxide. By M. Traube (*Ber.*, **19**, 1111—1114).—Hydrogen peroxide differs from the peroxides of manganese, lead, and silver in being formed during electrolysis at the negative pole and destroyed at the positive (Abstr., 1883, 283), in reducing all powerful oxidising agents, and in never being formed by

the oxidation of (palladium) hydrogen by oxygenated compounds or nascent oxygen. The author contends that it is never formed except in the presence of oxygen in the ordinary or molecular state, and therefore looks upon it as a compound of the oxygen molecule (as opposed to the atom) with two atoms of hydrogen, adopting Kekulé's idea that not only atoms but also molecules have the power of combining with one another, and extending this by assuming that an oxygen molecule possesses two valencies (over and above the two atomic valencies saturated in the molecule), which are capable of uniting with atoms. The author discusses the various results obtained by himself and others relative to the action and properties of hydrogen peroxide, and contends that these are all explained very much more satisfactorily by the above hypothesis than by the usually accepted formula.

L. T. T.

Oxygen Molecular Compounds. By M. Traube (*Ber.*, **19**, 1115—1117).—In this paper, the author extends his theory of the molecular structure of hydrogen peroxide (see preceding Abstract) to all those metallic peroxides (K, Na, Ba, Sr, Ca, Zn, Cd, Cu, Di) which contain an even number of oxygen-atoms and show analogous properties (such as the reducing action) to hydrogen peroxide. He proposes for such compounds (which belong to Schoenbein's class of antozonides) the name of *holoxides*. To this class the author refers oxyhæmoglobin, and he considers the fact that this substance gives up its oxygen under reduced pressure as a strong proof of his theory that in such compounds the oxygen is in molecular and not atomic combination.

L. T. T.

Change of Valency, and Combinations of Molecules with Atoms. By M. Traube (*Ber.*, **19**, 1117 — 1119).—The author attempts to explain the apparently varying valency of some elements by an extension of his theory of the constitution of hydrogen peroxide. He considers that many of the metals form two series of compounds, the one consisting of compounds of an atom of the metal with one or more atoms of a more negative element (or radicle); the other of compounds of a molecule of the metal with a negative radicle.

L. T. T.

Density of Liquefied Air and its Constituents: Atomic Volumes of Oxygen and Nitrogen. By S. Wroblewski (*Compt. rend.*, **102**, 1010—1012).—The density was determined by measuring the volume of the liquid and the volume of gas into which it expanded when the pressure was removed. The experiments with oxygen show that the density of the liquefied gas may be expressed by the equation $d = 1{\cdot}212 + 0{\cdot}00428T - 0{\cdot}0000529T^2$, in which T is the absolute temperature. This equation only holds good between the critical temperature $-118°$ and the boiling point of liquid oxygen in a vacuum, $-200°$. At the former temperature the density is 0·6, at the latter 1·24. It follows that the atomic volume of oxygen is less than 14. With nitrogen, the following numbers were obtained:—

Temperature.	Pressure in atmos.	Tension of saturated vapour in atmos.	Sp. gr. compared with water at 4°.	Coefficient of expansion.
— 146·6°	38·45	32·2	0·4552	—
— 153·7	30·65	20·7	0·5842	0·0311
— 193·0	1·00	1·0	0·83	0·007536
— 202·0	0·105	0·105	0·866	0·004619

At the critical point, the density is about 0·44, whilst at the moment of solidification it is about 0·9. The atomic volume of nitrogen is therefore very nearly 15·5. From these results it follows that in Mendeléeff's curve of atomic volumes there should be a minimum for oxygen between nitrogen and sodium.

Liquefied atmospheric air behaves as a mixture, the constituents of which obey different laws of liquefaction, and the composition of the liquid is therefore constantly changing. At the critical point, however, under a pressure of 45 atmos. and a temperature of —146·6°, the density is 0·59, whilst that calculated from the composition of the air is 0·6. C. H. B.

Atomic Volume of Oxygen. By E. H. Amagat (*Compt. rend.*, **102**, 1100).—The author has previously found (Abstr., 1885, 631) that, under a very high pressure, oxygen has the density 1·25 at a temperature of 17°. Wroblewski has recently shown (preceding Abstract) that at —200° under atmospheric pressure, the density is 1·24. It is probable that by combining high pressure with low temperature a still greater density, and consequently a smaller atomic volume will be obtained. In this case, it is most probable that, in accordance with Dumas' supposition, sulphur, selenium, and tellurium will have the same atomic volumes, whilst that of oxygen will have some simple ratio to the value for the other three. C. H. B.

Decomposition of Hypophosphoric Acid. By A. Joly (*Compt. rend.*, **102**, 1065—1068).—When crystals of the secondary hydrate $H_2PO_3 + H_2O$ are heated quickly to a temperature a little above their melting point (62°), they liquefy rapidly, but crystallise completely on cooling, and show no trace of decomposition. If, however, they are kept for some time at a temperature somewhat above 62°, the temperature of the fused substance rises to that of the bath, and it undergoes slow exothermic decomposition with formation of orthophosphoric and phosphorous acids. If the temperature of the fused mass is gradually raised, it loses water at a little above 100°, and at 180° gives off hydrogen phosphide, which is not spontaneously inflammable.

Crystals of the secondary hydrate, dried as carefully as possible and kept in sealed tubes, decompose slowly at the ordinary temperature into water, orthophosphoric acid and phosphorous acid. The dry crystals cannot be preserved in a dry vacuum, since they lose water and are converted into the normal hydrate. If they still contain some of the mother-liquor and are placed in a dry vacuum, they gradually decompose into orthophosphoric and phosphorous acids.

The composition of the crystals which separate from the last por-

tions of the mother-liquor varies, but approximates to that of the normal hydrate; whilst the composition of the liquid approximates to a mixture of orthophosphoric and phosphorous acids in equivalent proportions. The existence of the hydrate, $2H_2PO_3 + H_2O$, described by Sänger (this vol., p. 420), is improbable. The crystals obtained by Sänger probably consisted of the hydrate $H_2PO_3 + H_2O$, which had become partially dehydrated in the process of freeing it from the mother-liquor, or they may have been a mixture of the normal and secondary hydrates analogous to those which the author has constantly obtained when crystallisation has taken place in presence of a notable quantity of phosphoric and phosphorous acids.

If in the preparation of hypophosphoric acid all elevation of temperature is avoided and the solution evaporated rapidly in a dry vacuum, crystallisation begins when the composition of the liquid approaches $H_2PO_3 + 2H_2O$, and the crystals always have the composition $H_2PO_3 + H_2O$. C. H. B.

Behaviour of Thomas-slag with Water charged with Carbonic Anhydride. By M. A. v. Reis (*Chem. Zeit.*, **10**, 531—532) and T. Meyer (*ibid.*, 584).—Von Reis takes 5 grams of finely-powdered slag and digests it, with frequent shaking, in 500 c.c. of water, through which a current of carbonic anhydride is passing. From time to time the liquid is filtered off, and the residue is re-treated with fresh carbonic anhydride water. By treatment in this manner, a considerable amount of the slag, phosphoric acid, and silica pass into solution. The following results were obtained by treatment with 6 litres of water (see Table); whilst with 14 litres of water the dense slag (2) yielded 61·26 per cent. of soluble dry matter, containing 12·41 per cent. P_2O_5, and 7·55 per cent. silica; equal to 78·5 per cent. of the original P_2O_5, and 82·3 per cent. of the silica.

Quality of slag.	Original.		Per cent. dry matter dissolved.	Insoluble dry matter.	
	Per cent. P_2O_5.	Per cent. SiO_2.		Per cent. P_2O_5.	Per cent. SiO_2.
Dense slag (1)	15·80	9·05	33·92	5·86	3·88
Dense slag (2)	15·61	9·10	34·76	6·04	3·76
Slag full of small bubbles....	16·38	7·80	31·60	5·12	2·99
Slag full of large bubbles....	14·71	6·40	31·00	5·96	3·22

T. Meyer, experimenting on this subject, digested 2 grams of finely-powdered slag containing 20·2 per cent. P_2O_5 and 54·0 per cent. CaO, with 8 litres of water saturated with carbonic anhydride, for 50 hours, shaking about 20 times, and obtained in solution 53·6 per cent. of the total phosphoric acid and 57·8 per cent. of the calcium oxide. These results confute the statement that the phosphoric acid in this slag was insoluble, or would not dissolve until the excess of lime was got rid of. T. Meyer, in a parallel experiment with Lahn

phosphate containing 20·6 P_2O_5, obtained 14·7 per cent. of the phosphoric acid in solution. D. A. L.

Combustion of Carbonic Oxide. By L. Meyer (*Ber.*, **19**, 1099—1106).—Since the publication of Dixon's detailed experiments, the author, in conjunction with W. Stahl, has repeated Bötsch's experiments and has obtained results concordant with those described by Dixon (Trans., 1886, 94), finding that if sufficiently well dried, a mixture of carbonic oxide and oxygen is only exploded when a very powerful spark and a tolerably high gas pressure are employed.
L. T. T.

Action of Air, Silica, and Kaolin on Haloïd Salts of the Alkalis. By A. Gorgeu (*Compt. rend.*, **102**, 1164—1167).—Alkaline chlorides and bromides heated to cherry-redness in a current of dry air lose 0·1 per cent. of their weight. Under the same conditions, potassium iodide loses about 0·6 per cent., and the decomposition of sodium iodide is still greater. In moist air, the chlorides and bromides lose 0·3—0·6 per cent., potassium iodide 1·5—2·0, and sodium iodide 5·0—7 0 per cent.

Sand and ignited silica have scarcely any action on fused chlorides in dry or moist air, but anhydrous kaolin acts more readily. Hydrated silica has more action than anhydrous silica, especially in presence of moist air, and hydrated kaolin decomposes a considerable proportion of the chlorides. The bromides are somewhat more easily attacked, and the iodides are far more readily decomposed, the potassium salt being the more stable in both cases. Reactions similar to these probably take place during volcanic action, and are the cause of the presence of hydrochloric acid, &c., in the fumerolles.

If a mixture of alkaline chlorides and iodides is fused with clay in presence of water vapour, the iodide is completely and somewhat rapidly decomposed. If alkaline bromides or calcium chloride are substituted for the iodide no such preferential decomposition is observed, but magnesium chloride under the same conditions is decomposed completely and somewhat rapidly before the alkaline chlorides. It follows from these results that *sal gem* of volcanic origin will be free from iodine and magnesium chloride. The absence of these substances has been proved in the case of the sal gem from Dieuze.

Hydrochloric acid can be obtained somewhat easily by heating salt to dull redness with excess of kaolin in presence of water vapour, and chlorine is obtained by heating salt with anhydrous kaolin in dry air, but it is improbable that these processes will have any immediate practical value. The production of iodine is however readily effected by heating an alkaline iodide to dull redness with kaolin in ordinary air. Under these conditions kaolin will decompose its own weight of potassium iodide in an hour. C. H. B.

Potassium Nitrate and Chlorate. By H. Beckurts (*Arch. Pharm.* [3], **24**, 333—337).—The author concludes that almost all commercial potassium nitrate contains small quantities of potassium chlorate or perchlorate. In one case 0·0674 per cent. was found as

determined by the difference in weight of silver chloride precipitated before and after ignition of the nitrate. J. T.

Dimorphism of Hydrogen Potassium Sulphate. By WYROUBOFF (*Jahrb. f. Min.*, 1886, i, Ref., 391—392).—The compound $HKSO_4$ crystallises in the rhombic system. Marignac suggested that it is dimorphous, as on crystallisation by cooling or from highly acid solutions, white fibrous silky masses are produced. If a hole is made in these fibres with a glass rod, rhombic crystals are obtained. These fibres, which cannot be freed from the excess of acid, are very similar to the misenite of Scacchi, a mineral from Cape Misenum near Naples. The author now clearly proves that hydrogen potassium sulphate is dimorphous. By slow evaporation of a solution of the salt, he obtained long, acicular, monoclinic crystals, with the axial ratio $a : b : c = 3{\cdot}2169 : 1 : 2{\cdot}1842$; $\gamma = 77° 55'$. The sp. gr. is 2·245 (for the rhombic salt, the author found 2·273). The plane of the optic axes is parallel to the plane of symmetry. The positive bisectrix makes an angle of 17° with a normal to 0P, and 60° 55′ with one to $\infty P\frac{4}{3}$. Misenite is stated to belong to the monoclinic system.

B. H. B.

Combination of Zinc Chloride with Hydrogen Chloride. By R. ENGEL (*Compt. rend.*, **102**, 1068—1071).—When dry hydrogen chloride is passed into a solution of zinc chloride containing fragments of metallic zinc until the sp. gr. of the liquid at about 25° approaches 2, care being taken to prevent too great a rise of temperature, deliquescent, rhombic crystals of the composition $2ZnCl_2,HCl + 2H_2O$ separate. These crystals are stable in dry air at the ordinary temperature, and can be kept in well corked flasks, but in a dry vacuum, or when heated, they decompose with loss of water and hydrogen chloride and formation of anhydrous zinc chloride. At 100°, the crystals lose hydrogen chloride, but a definite hydrate is not formed. The product is a liquid containing a solid in suspension, and they remain separated even when completely cooled. The solid is *anhydrous zinc chloride;* the liquid is a concentrated aqueous solution of zinc chloride containing some hydrochloric acid.

After the first separation of the crystals just described, the mother-liquor will absorb a further quantity of hydrogen chloride, with production of a further quantity of crystals of the same composition, and it is only after several crops of these crystals have been obtained that the liquid becomes saturated with hydrochloric acid. If now the liquid is cooled to 0° it deposits long needles of the composition $ZnCl_2,HCl + 2H_2O$, which are very unstable and lose hydrogen chloride when placed in dry air, the first compound, $2ZnCl_2,HCl + 2H_2O$, being formed. C. H. B.

Hydrates of Zinc Chloride. By R. ENGEL (*Compt. rend.*, **102**, 1111—1113).—When an aqueous solution of zinc chloride containing 70·5 per cent. of the salt is cooled at 0° for 24 hours, it deposits somewhat large crystals which melt at 7° and have the composition $ZnCl_2 + 3H_2O$. This hydrate is extremely soluble in water, one part of the latter dissolving about 12·5 parts of the crystals at 0°.

If a solution containing 79·9 per cent. of the chloride is cooled at 0° for a long time, it solidifies completely. At 16°, the crystalline mass melts partially, and if the liquid is carefully poured off, a residue of infusible crystals is left. The fusible portion has the composition $ZnCl_2 + 2H_2O$, and the crystals which do not melt at 16° have the composition $2ZnCl_2 + 3H_2O$. This last hydrate is also obtained in bulky crystals when a solution of zinc chloride is allowed to evaporate over phosphoric anhydride.

Two of the hydrochlorides of zinc chloride previously described (preceding Abstract) may be regarded as formed from the first and last hydrates respectively by the displacement of a molecule of water by hydrogen chloride, thus: $ZnCl_2 + 3H_2O$ and $ZnCl_2,HCl + 2H_2O$, $2ZnCl_2 + 3H_2O$ and $2ZnCl_2,HCl + 2H_2O$. C. H. B.

Modifications of Cupric Oxide. By Joannis (*Compt. rend.*, **102**, 1157—1164).—Cupric oxide prepared at a low temperature dissolves readily in dilute acids, whereas cupric oxide which has been strongly ignited dissolves slowly even in boiling concentrated acids. In order to determine the heats of formation of the two modifications, they were dissolved in a solution of ammonium iodide acidified with hydrochloric acid. This method does not give absolute values, but serves to determine with sufficient accuracy the difference between the heats of formation of the two varieties. The following results were obtained:—

	Heat developed.
Oxide prepared by strongly heating cupric nitrate ..	8·09 cal.
„ „ „ „ sulphate ..	8·03 „
„ at a low temperature	9·11 „

It follows that the difference between the heats of formation is about 1 cal., a difference similar to that corresponding with the conversion of the diamond into charcoal or vitreous selenium into metallic selenium.

Cupric oxide prepared at a low temperature retains water very tenaciously, but can be dried in a vacuum at 440°. Some thermal measurements made as above indicate that the water which is retained is actually in combination with the oxide. C. H. B.

Fluorescence Spectra Zα and Zβ. By L. de Boisbaudran (*Compt. rend.*, **102**, 899—902).—The fluorescence spectra provisionally distinguished as Zα and Zβ are in all probability due to two distinct substances. This conclusion rests mainly on the facts that the substance giving the spectrum Zα is found in greatest proportion (with respect to the substance giving the spectrum Zβ) in the first fractions precipitated by ammonia and in the last fractions precipitated by potassium sulphate or hydrochloric acid; that the intensities of the two spectra do not vary in the same degree under identical conditions, and that the addition of various substances such as ruthenium, platinum

or ferric chlorides, samarium, &c., to the solutions giving the two spectra produces very different effects upon each of them.

C. H. B.

Gadolinium, the Y_α of Marignac. By L. de Boisbaudran (*Compt. rend.* **102**, 902).—In a note to the author, Marignac gives the name *Gadolinium* (Gd) to the substance which has hitherto been provisionally distinguished as Y_α. C. H. B.

Holmium, or Soret's X. By L. de Boisbaudran (*Compt. rend.*, **102**, 1003—1004).—The spectrum of holmium as described by Soret contains bands in the following positions: 8040, 7530, 6404, 5363, 4855. 4755, 4530—4490, 4300, 4145, 3890—3870. By fractionating repeatedly with ammonia and potassium sulphate, the author has obtained earths which show the bands at 7530 and 4515 very distinctly, whilst the bands at 6404 and 5363 are entirely absent, and others which show the 6404 and 5363 very distinctly, whilst 7530 and 4515 are feeble. It is evident, therefore, that the spectrum attributed to holmium is due to at least two distinct substances. The author proposes to retain the name holmium for the substance which gives the bands 6404 and 5363, and he gives the name *dysprosium* to the substance characterised by the bands 7530 and 4515. C. H. B.

Dysprosium. By L. de Boisbaudran (*Compt. rend.*, **102**, 1005—1006).—The earths which do not show the bands of holmium but give the bands of dysprosium are relatively rich in terbia, but the bands 7530 and 4515 cannot be attributed to this element, since they are strongest with the palest coloured oxides in which the proportion of terbia is lowest. Neither are they due to erbium, samarium, or didymium, for they are absent from the spectra of the purest specimens of these substances. The following bands show the same relative variations in intensity, and may be attributed to dysprosium, with the doubtful exception of 8040:—(?) 8040, 7565 (somewhat narrow), 4750 (broad and very nebulous), 4515 (nebulous at the edges), and 4275 (somewhat broad). C. H. B.

Aluminium Potassium Silicate and Aluminium Sodium Silicate. By A. Gorgeu (*Compt. rend.*, **102**, 1108—1110).—When kaolin is fused with an excess of haloïd alkaline salt until evolution of vapours ceases, a product is obtained which is insoluble in cold water but soluble in dilute acids. This product is a compound of a normal silicate, $2SiO_2,Al_2O_3,K_2O$, with a quantity of the haloïd salt varying from 1·5 to 6 per cent. In most cases, it is obtained in the form of amorphous, monofractive grains even when the mass has been completely fused. If, however, kaolin is fused with 20 parts of sodium iodide, birefractive prisms rapidly attacked by alcohol and water are obtained. They consist of the normal silicate combined with at least one-quarter of an equivalent of sodium iodide. All these compounds are slightly attacked by cold water and more readily by boiling water, but are not dissolved by solutions of caustic alkalis or alkaline carbonates.

If kaolin is fused with 10 parts of potassium carbonate in presence of moist air at a cherry-red heat, it yields a silicate of the composition

$2SiO_2,Al_2O_3,K_2O$, analogous to anorthite and free from excess of alkaline salt. If, however, the mixture is raised slowly to a pale orange-red heat and kept at this temperature for some time, the product is a silicate in which the oxygen ratios are 1 : 1·4 : 0·45. It is insoluble in cold water, crystallises in small octahedra, and is a bibasic silicate mixed with a small quantity of the silicate formed at a cherry-red heat.

The silicate produced by sodium carbonate at a cherry-red heat forms birefractive prismatic crystals which are converted by washing with water into broken lamellæ and monorefractive grains. The part insoluble in water has the composition $3SiO_2,2Al_2O_3,3Na_2O$. The silicate produced at bright redness forms birefractive prismatic crystals very readily attacked by water. The oxygen ratio agrees with the formula SiO_2,Al_2O_3,Na_2O.

When 10 parts of potassium hydroxide is fused with kaolin, the product is the same both below dull redness and at a cherry-red heat, but the quantity insoluble in water diminishes the higher the temperature. The operation should therefore be stopped as soon as the kaolin has been converted into octahedra. The oxygen ratios of the silicate thus obtained are 1 : 1·73 : 0·73.

Fused sodium hydroxide acts very rapidly on kaolin, and it seems impossible to obtain a homogeneous and completely crystallised product. In the best specimen the oxygen ratios were 1 : 0·85 : 0·65. All the basic silicates obtained by the action of the alkaline hydroxides on kaolin are soluble in dilute acids, and insoluble in boiling solutions of alkaline carbonates, but differ from the normal silicates by their solubility in solutions of alkaline hydroxides and the ease with which they are attacked by water. C. H. B.

Chemical Behaviour of Iron in the Magnetic Field. By E. L. Nichols (*Amer. J. Sci.*, **31**, 272—283).—The author describes a set of experiments with aqua regia, nitric acid, hydrochloric acid, and sulphuric acid, to illustrate the phenomenon that when finely divided iron is placed in a magnetic field of considerable intensity and exposed to the action of the acid, the chemical reaction differs in several respects from that which occurs under ordinary circumstances.

With aqua regia, it was found that the speed of reaction is greater in the magnetic field than without, and that the heat of chemical union is much greater. The production of nitrous fumes under the influence of the magnet, and the yellow colour of the resulting solution, show that the reaction was modified in chemical character. With nitric acid, the effect of the magnet was to greatly increase the speed, reducing the average time from eight minutes to less than one minute. Red fumes always resulted from the action within the field. With hydrochloric acid, the rise of temperature was much smaller than in the experiments with aqua regia and nitric acid; the speed of reaction within the magnetic field differed very little from that occurring under ordinary circumstances; and the character of the reaction in the two cases was almost identical. The rise of temperature under the influence of the magnet, however, was found to be slightly in excess of that produced when the magnet was not in action.

With sulphuric acid, the reaction was uniform and complete, and apparently of the same chemical character within and without the field. The magnet was found, however, to increase the speed of reaction, and to decrease the amount of heat produced.

A series of measurements were made with nitric acid, in which powdered copper was substituted for iron. The reaction in the field was found to be identical with that which occurred when the magnet was not in action.

The results arrived at by the author are shown in a series of curves; the ordinates denoting temperature in degrees centigrade, and the abscissæ time in minutes. The experiments are preliminary to a more complete investigation of the novel series of effects developed.

B. H. B.

Conversion of Chromous Chloride into Chromic Chloride: Solution of Anhydrous Chromic Chloride. By RECOURA (*Compt. rend.*, **102**, 921—924).—If a dilute solution of chromous chloride is oxidised to Cr_2Cl_4O and then treated with hydrochloric acid, little or no action takes place, but if a saturated solution of chromous chloride is first oxidised and is then saturated with gaseous hydrogen chloride, the grey-blue variety of chromic chloride, $Cr_2Cl_6 + 13H_2O$ (this vol., p. 508), is precipitated. When the process is reversed and a current of air or oxygen is passed into a cooled mixture of chromous chloride and concentrated hydrochloric acid, a green solution is obtained, and if this is treated with a current of hydrogen chloride the green variety of chromic chloride (*loc. cit.*) is precipitated.

When hydrogen chloride is passed into an aqueous solution of crystallised chromic chloride part of the salt is precipitated, and if the current of gas is continued for several days the colour of the solution changes and ultimately becomes reddish-brown. The solutions of chromic chloride obtained by the above reactions become brown almost immediately when treated with hydrogen chloride. The brown solution becomes green again when diluted. It doubtless contains a hydrochloride of chromic chloride, which, however, could not be isolated on account of its great solubility.

When chlorine free from oxygen is passed into a dilute solution of chromous chloride, a somewhat dichroic solution of chromic chloride is obtained identical in its properties with a solution of the green variety partially converted into the grey-blue variety. A solution with exactly the same properties is obtained when anhydrous chromic chloride is dissolved in water containing a trace of a chromous salt or any reducing chloride.

This observation supports Loewel's hypothesis, that the trace of chromous chloride in solution is converted into soluble chromic chloride at the expense of the anhydrous chloride, a portion of the latter being reduced to chromous chloride, which in its turn becomes soluble chromic chloride at the expense of another portion, and so on until the whole is converted into the soluble variety. The reducing chlorides probably act by reducing a small quantity of the chromic chloride to the chromous salt, with the result just described.

C. H. B.

Compounds of Fluorides of Heavy Metals with Ammonium, Potassium, and Sodium Fluorides. By R. Wagner (*Ber.*, **19**, 896—898).—The double salts, $SnF_2,2NH_4F + 2H_2O$, $3SnF_2,2KF + H_2O$, and $3SnF_2,2NaF$, were prepared by saturating acid solutions of the respective alkaline fluorides with freshly precipitated stannous hydrate.

$Cr_2F_6,6NH_4F$; $Cr_2F_6,4KF + 2H_2O$ and $Cr_2F_6,4NaF + H_2O$ were obtained by mixing solutions of the constituents. A second ammonium salt, $Cr_2F_6,4NH_4F + 2H_2O$, was prepared by passing ammonia into an aqueous solution of chromic fluoride, shaking out the solution with absolute alcohol, and dissolving the mass so obtained in aqueous hydrofluoric acid; it forms emerald-coloured octahedra. The zinc salts, ZnF_2,KF; ZnF_2,NaF, and $ZnF_2,2NH_4F + 2H_2O$ were prepared.

The double ammonium and iron fluoride, $Fe_2F_6,6NH_4F$, described by Marignac, was prepared by nearly neutralising a solution of ferric fluoride in hydrofluoric acid with ammonia and evaporating. The potassium salt, $Fe_2F_6,6KF$, mentioned by Berzelius, and the salt, $Fe_2F_6,6NaF$, were obtained by adding a solution of ferric fluoride to an excess of solutions of potassium and sodium fluorides respectively; they are both white. Two double salts were obtained with ammonium fluoride and ferrous fluoride, $FeF_2,NH_4F + 2H_2O$ and $FeF_2,2NH_4F$, the one forms green octahedra, the other is brown. The potassium salt, $FeF_2,KF + 2H_2O$, is a flesh-coloured substance; the anhydrous salt described by Berzelius could not be obtained.

The following double fluorides of nickel and cobalt, with the fluorides of the alkali metals, were prepared by mixing the corresponding solutions: $CoF_2,2NH_4F + 2H_2O$; $CoF_2,KF + H_2O$; $CoF_2,NaF + H_2O$ (these are rose-coloured); $NiF_2,KF + H_2O$ and $NiF_2,NaF + H_2O$ (both these are sulphur-coloured), and $NiF_2,2NH_4F + 2H_2O$ (pale green). N. H. M.

Double Titanium Fluorides. By A. Piccini (*Gazzetta*, **16**, 104—107).—On adding potassium hydrogen fluoride to the liquid obtained by treating titanium trichloride with water, a dark violet precipitate of a double fluoride, $TiF_3,2KF$, is produced. It is sparingly soluble in water, but soluble in dilute acids, forming green solutions, which yield with alkalis an azure-blue precipitate, gradually transformed into titanic acid on exposure to air. If ammonium fluoride is used, one of two salts is obtained, according as the fluoride is added to the titanium chloride, or conversely; in the latter case, the double salt has the composition $TiF_3,3NH_4F$, but in the former $TiF_3,2NH_4F$. In their general properties, these ammonium salts resemble those of potassium; the former gradually loses its colour on exposure to the air, and is converted into an oxyfluoride of composition $TiO_2F_2,3NH_4F$. V. H. V.

Combination of Phosphoric Acid with Titanic, Zirconic, and Stannic Acids. By P. Hautefeuille and J. Margottet (*Compt. rend.*, **102**, 1017—1019).—The authors have previously shown (Abstr., 1885, 120) that phosphoric acid dissolves silica with the formation of silicon phosphate. Phosphoric acid, H_3PO_4, melted at a temperature below that at which it loses water, also dissolves

hydrated titanic, zirconic, and stannic oxides, although these compounds are much less soluble than silica. When the phosphoric acid is dehydrated slowly or rapidly, the corresponding phosphates are precipitated in highly refractive octahedra, or cubo-octahedra, which have no action on polarised light. The crystals form more readily in presence of a trace of alkali. Their composition is analogous to that of silicon phosphate, and they have the formulæ TiO_2,P_2O_5; ZrO_2,P_2O_5; and SnO_2,P_2O_5, respectively. Zirconic phosphate is not attacked by concentrated acids, or by potassium hydrogen sulphate, but is readily decomposed by fused alkaline carbonates with formation of a soluble phosphate and an insoluble alkaline zirconate. If this reaction is employed to separate zirconia from phosphoric acid, fusion should take place at the lowest possible temperature, otherwise a zirconate is formed insoluble in acids. The cooled mass is treated with water and the residue first washed with dilute soda solution, and afterwards with dilute ammonia containing ammonium nitrate. The zirconate is then dissolved in hydrochloric or sulphuric acid, and the zirconium precipitated by the addition of ammonia.

The titanium phosphate was analysed in the same way. The tin phosphate was fused with sodium carbonate and sulphur, as in the analysis of cassiterite. C. H. B.

Ammonium Vanadates. By A. Ditte (*Compt. rend.*, **102**, 918—921).—*Normal ammonium vanadate*, $(NH_4)_2V_2O_6$, is always formed when vanadic acid is brought in contact with an excess of ammonia, and is characterised by its insolubility in a saturated solution of ammonium chloride. It dissolves in 100 parts of cold water, but is more soluble in boiling water, by which it is decomposed with ultimate formation of the trivanadate, which separates in brilliant yellow plates. A hot saturated solution of the normal vanadate containing a sufficient excess of ammonia to keep it colourless, deposits brilliant, colourless, highly refractive, hexagonal prisms terminated by very acute, elongated pyramids. These crystals leave a residue of the tri- and tetr-oxides when heated in a closed vessel.

Ammonium sesquivanadate, $3V_2O_5,2(NH_4)_2O$, is obtained in transparent, ruby-red, monoclinic crystals, together with yellow crystals of the oxalovanadate, by saturating a solution of ammonium oxalate (saturated at 30°) with soluble vanadic anhydride and evaporating the orange-red liquid in a vacuum. These crystals are very soluble in cold water; they contain 4 or 6 mols. H_2O according to the temperature at which they are formed. They lose this water when gently heated, and become red; at a higher temperature, they decompose completely.

Ammonium bivanadate, $(NH_4)_2O,2V_2O_5$, is obtained in bulky, garnet-red, monoclinic crystals by adding a small quantity of acetic acid to a boiling saturated solution of the normal salt, and evaporating in a vacuum at the ordinary temperature. The crystals give an orange-yellow powder which loses water and becomes red when heated, eventually decomposing completely and leaving a residue of vanadic anhydride. They dissolve readily in cold water, forming a red solution which decomposes when boiled and deposits the trivanadate.

Ammonium trivanadate, $(NH_4)_2O,3V_2O_5$, is obtained in thin, transparent, yellow, octagonal plates by boiling an aqueous solution of any of the preceding compounds, and also very readily by adding *an excess* of acetic acid to a solution of a normal salt and evaporating the liquid. When gently heated, the crystals become vermilion without loss of weight, and resume their original colour on cooling, but they decompose below a red heat and leave a greenish-yellow powder of pure vanadic anhydride. This is the most readily formed and the most stable of all the acid ammonium vanadates. It is only slightly soluble in cold and hot water, and is not decomposed when boiled with water for several hours. If acetic acid is added to a cold saturated solution of the normal vanadate until the precipitate at first formed redissolves, and the deep-red solution is evaporated in dry air at the ordinary temperature, it deposits dull deep-red crystals of the hydrated trivanadate, $(NH_4)_2O,3V_2O_5 + 5H_2O$. These crystals are only slightly soluble in cold water, but dissolve readily in ammonia with formation of the normal salt. The amount of water which they contain varies with the conditions of crystallisation. C. H. B.

Action of Vanadic Acid on Ammonium Salts. By A. Ditte (*Compt. rend.*, **102**, 1019—1022 and 1105—1107).—Soluble vanadic anhydride acts on solutions of ammonium salts in three ways. If the vanadic anhydride can unite with the acid of the particular salt, an ammonium salt of a complex acid is formed. Solutions of these salts are generally coloured and are only slowly decolorised on adding excess of ammonia. In other cases, the vanadic anhydride decomposes the ammonium salt with formation of an acid ammonium salt and an ammonium vanadate, whilst in the case of certain ammonium salts no sensible decomposition takes place.

Ammonium Phosphate.—A warm solution of this salt dissolves a large quantity of vanadic anhydride and forms a deep red, almost black solution which deposits deep garnet-red crystals which are octahedra with truncated summits or rhomboidal plates with an angle closely approaching 90°. Both the solution and the crystals lose their colour and become pale-yellow when heated, but resume their original colour on cooling. When the crystals are more strongly heated, they decompose with evolution of water and ammonia. They have the composition $4V_2O_5,P_2O_5,3(NH_4)_2O + 16H_2O$, and dissolve readily in water.

If the mother-liquor from these crystals is concentrated by boiling, it becomes pale-yellow, but on cooling becomes red again and deposits some red crystals. After some time, however, the liquid deposits a considerable quantity of small, greenish-yellow, hexagonal prisms, terminated by very obtuse pyramids. They have the composition $2V_2O_5,4P_2O_5,5(NH_4)_2O + 24H_2O$, and dissolve readily in cold water. When gently heated, they lose water, and at a higher temperature decompose.

A third compound is obtained by dissolving yellow ammonium trivanadate in an excess of a warm solution of ammonium phosphate. The greenish-yellow solution thus obtained remains supersaturated even when highly concentrated, but if a particle of the solid matter

which always forms on the sides of the vessel is allowed to drop into the liquid, an abundant crop of transparent, citron-yellow, very soluble crystals of the composition $3V_2O_5,2P_2O_5,5(NH_4)_2O + 24H_2O$ is obtained. When gently heated, they lose water with great intumescence and leave a grey residue which melts to a black glass at a red heat.

Ammonium Arsenate.—A boiling solution dissolves a considerable quantity of vanadic anhydride, forming a pale orange liquid which deposits brilliant, transparent, citron-yellow plates of the composition $2V_2O_5,4As_2O_5,5(NH_4)_2O + 18H_2O$; these dissolve readily in water, and when heated alone they first lose water and then decompose.

Ammonium Molybdate.—A warm solution dissolves a large quantity of vanadic anhydride, forming a deep-red liquid which deposits brilliant, white, silky, channelled needles of the composition $2V_2O_5,4MO_3,3(NH_4)_2O + 9H_2O$. They decompose when heated and dissolve readily in water, forming an orange-yellow solution.

Ammonium Tungstate.—A boiling solution saturated with vanadic anhydride forms a deep garnet-red solution which when highly concentrated deposits brilliant octahedra of the composition $V_2O_5,5WO_3,2(NH_4)_2O + 10H_2O$. They are extremely soluble in cold water, and when heated they decompose leaving a residue which does not melt at a red heat.

Ammonium di-iodate solution dissolves a small quantity of vanadic anhydride, and the yellow liquid deposits orange-yellow, short, flattened prisms of the composition $2V_2O_5,5I_2O_5,3(NH_4)_2O + 20H_2O$. The crystals are very soluble in cold water, and when heated they lose water and yield a brilliant red, lustrous substance which decomposes on further heating.

Ammonium Oxalate.—A warm concentrated solution dissolves a large quantity of vanadic anhydride, and the deep-red liquid first deposits garnet-red crystals of ammonium sesquivanadate, and then large, pale-yellow, monoclinic prisms, very soluble in water. They have the composition $3V_2O_5,8C_2H_2O_4,8(NH_4)_2O + 12H_2O$, and when gently heated they lose water and form a greyish-red substance which decomposes when more strongly heated. If the original solution is concentrated by heating, carbonic anhydride is evolved and some vanadic acid is reduced.

Ammonium *borate*, ammonium *acetate*, and ammonium *sulphate* solutions when heated with vanadic anhydride yield ammonium trivanadate, and either an acid ammonium salt or the free acid. Ammonium iodate yields the trivanadate and a small quantity of ammonium di-iodate, which then acts on the vanadic anhydride with formation of the compound described above. Ammonium *vanadate* in cold solution forms the divanadate, but a hot solution forms the trivanadate.

Ammonium Chromate.—A warm solution dissolves a considerable quantity of vanadic anhydride, and the deep-red solution saturated at 60° and concentrated in a vacuum at the ordinary temperature deposits small crystals of the composition $V_2O_5,2CrO_3,2(NH_4)_2O + 7H_2O$. If, however, the solution is concentrated at a temperature above 60°, ammonium trivanadate separates and the liquid afterwards

deposits ammonium dichromate. It follows therefore that below 60° ammonium chromate behaves like the salts of the first group, whilst above 60° it behaves like a salt of the second group.

Ammonium *nitrate* and *perchlorate* solutions do not dissolve vanadic anhydride to an appreciable extent, but when boiled with it they gradually convert the soluble into the insoluble variety. Ammonium *chloride* has very little action, but a small quantity of ammonium trivanadate is formed and a small quantity of vanadic anhydride is reduced owing to the partial dissociation of the chloride with liberation of ammonia and hydrochloric acid. *Ammonium carbonate* in a cold solution yields ammonium bivanadate with an excess of vanadic anhydride, but with excess of ammonium carbonate the normal vanadate alone is formed even in hot solutions.

C. H. B.

Mineralogical Chemistry.

Occurrence of Diamonds in Borneo. By T. Posewitz (*Jahrb. f. Min.*, 1886, i, Ref., 432—433).—Diamonds occur in Borneo, in association with gold, platinum, magnetite, and corundum, in alluvial and diluvial deposits. The diamonds are confined to several districts near the coast in the western and south-eastern portion of the island. The diluvial deposits are 0·5 to 8 metres thick, and consist of quartz, and diorite-, syenite-, and gabbro-débris. The mother-rock of the diamond is unknown. The occurrence of blue corundum is regarded as a favourable indication, whilst with blackish-brown grains of very hard diamond, the finding of stones fit for cutting is out of the question. Of the coloured diamonds, the bluish variety is the most highly valued. The production of diamonds at the beginning of this century was considerable. It has now, however, become reduced to a minimum.

In conclusion, the author notes that the celebrated 367-carat diamond of the Sultan of Matan is really quartz. B. H. B.

Native Bismuth from Sweden. By L. J. Igelström (*Jahrb. f. Min.*, 1886, i, Ref., 398—399).—The author notes the occurrence of native bismuth and bismuth glance, with copper pyrites in the parish of Säjsnäs in Dalecarlia. The minerals form amorphous patches in a brownish-red mass of garnet. B. H. B.

Liquid Inclusions in Brazilian Topaz. By N. v. Nordenskiöld (*Jahrb. f. Min.*, 1886, i, Mem., 242—244).—The author brings forward a number of arguments to oppose the view generally held that the fluid enclosed in topaz (termed by Dana "brewsterlinite") is liquid carbonic anhydride.* The crystallised topaz from the granite beds of Brazil must, in all probability, have been originally derived from small pegmatite veins that were not of plutonic origin. The crystals, like the Swiss quartz crystals, probably crystallised out from aqueous

* *Note by Editor.*—The author does not seem to be acquainted with Hartley's investigations relating to this subject (see *Chem. Soc. J.*, 1876, i, 137; ii, 237; and 1877, i, 241).

solutions percolating through fissures in the veins. The pressure in the mother-liquid could not have been sufficiently great for carbonic anhydride to be present in a liquid state. The physical properties of the enclosed fluid certainly do not agree with those of liquid carbonic anhydride. And it must be assumed that the physical properties of liquid substances in microscopical cavities are the same as those observed in experiments with large quantities.

With reference to Vogelsang's and Geissler's analyses, the author is of opinion that these show conclusively that the liquid contains carbon and hydrogen; and are no evidence that it consists of liquid carbonic anhydride.

If a fragment of white or blue topaz from Brazil, containing these cavities, is heated, it usually decrepitates, although not violently. It splits up into thin plates, which after heating for a short time in air become red; grey on heating in hydrogen; and colourless after continued heating in air. On examining these plates under the microscope, it is found that the larger cavities, previously filled with liquid, have burst and are quite empty; whilst several of the smaller ones are still filled with one liquid, in which, as was previously the case, a movable bubble may be observed, which disappears when slightly heated. Brewster's second fluid is not to be seen. The majority of the unemptied cavities, after heating, do not contain a liquid, but a granular black or reddish-brown substance, resembling the carbon left after the ignition of resinous organic substances. This reaction indicates that the liquid substance could not have been carbonic anhydride, but must have been an organic compound, probably a hydrocarbon of the naphtha-group. This hypothesis is fully in accordance with the occurrence of asphalt in cavities lined with crystals in crystalline rocks; as well as with the occurrence of organic substances in numerous minerals (*e.g.*, emerald, citrine, various red and green felspars, smoky quartz) formed in the same way as the Brazilian topaz. B. H. B.

Analyses of Emery. By R. Jagnaux (*Jahrb. f. Min.*, 1886, i, Ref., 393).—The author analysed three varieties of emery, with the following results:—

	Naxos.	Tyre.	Smyrna.
Corundum	64·2	55·8	56·1
Silica	2·0	7·2	7·0
Magnetite	26·8	17·5	11·0
Ferric oxide	6·9	19·5	25·9
	99·9	100·0	100·0

B. H. B.

Manganite from Oberstein. By R. Brauns (*Jahrb. f. Min.*, 1886, i, Mem., 252—253).—The crystals described were found in an agate amygdaloid with goethite and quartz, near Oberstein. They are all small. The largest is 10 mm. in the direction of the vertical axis, 2 mm. in the direction of the macrodiagonal. The colour is steel-grey, with brown streak. The crystals occur isolated on the quartz. The following planes were observed: $\infty P\bar{\infty}$, ∞P, $\infty P\frac{5}{2}$, $0P$, $\frac{1}{2}\frac{7}{0}P\bar{\infty}$.

Of these planes, the last is new for manganite. The axial ratio is $a : b : c = 0{\cdot}8441 : 1 : 0{\cdot}5448$. B. H. B.

Fusibility of Calcium Carbonate. By A. Becker (*Jahrb. f. Min.*, 1886, i, Ref., 403—404).—The author has repeated the experiments of Hall and G. Rose of heating calcium carbonate in a closed space, air being excluded, and shows that calcium carbonate (aragonite, calcite, chalk, precipitated calcium carbonate), even at a low pressure, is changed to crystalline rhombohedral calcium carbonate, without fusion ensuing. B. H. B.

Xenotime from Minas Geraes, Brazil. By H. Gorceix (*Compt. rend.*, **102**, 1024—1026).—Crystals of xenotime, sometimes entire, sometimes tarnished and rounded, are found in considerable quantities in the washings from the diamond workings at Dattas, to the south of Diamantina, in the basin of Rio São Francisco, and at other localities in the same district. They are sometimes as much as 10 mm. in length, and their form is a square prism terminated by a pyramid with double positive refraction. Measurements of the angles gave the following results: b, b, opposed, 97° 30′; b, b, adjacent, 124° 26′; b'_m 131°; $b : h :: 115 : 100$. Cleavage easy along the plane m; hardness 5; sp. gr. at 20° = 4·6. When heated to bright redness the crystals become white without loss of weight. Analysis shows that they have the composition P_2O_5, 35·71; $Y_2O_3 + Er_2O_3$, 63·48. Insol. res. 0·62 = 99·81. Leaving out the insoluble matter, which is mainly silica, the composition of xenotime is P_2O_5, 35·8; $Y_2O_3 + Er_2O_3$, 64·2, which agrees with the formula $(Y_2O_3,Er_2O_3)P_2O_5$, one-sixth of the bases being erbia. The erbia separated from the mineral in the usual way has a rose colour, and gives the erbium spectrum described by Thalén. The light reflected from the brilliant surfaces of the original crystals gives absorption-bands in the green and the blue, but no distinctly visible absorption in the yellow. Xenotime dissolves completely in warm sulphuric acid, but somewhat less readily than monazite. It contains neither zirconium, titanium, cerium, nor didymium. C. H. B.

Minerals from Kangerdluarsuk, in Greenland. By J. Lorenzen (*Jahrb. f. Min.*, 1886, i, Ref., 404—405).—*Liëvrite.*—The author found the axial ratio $a : b : c = 0{\cdot}674367 : 1 : 0{\cdot}418449$. The following planes were observed: P, $4\breve{P}2$, $\infty\breve{P}2$, $\infty\bar{P}2$, $\bar{P}\infty$, $2\breve{P}\infty$, and various high brachydomes and pyramids.

Rinkite.—Monoclinic; $a : b : c = 1{\cdot}56878 : 1 : 0{\cdot}292199$; $\beta = 88° 47'$. Analysis gave the following results:—

F.	SiO_2.	TiO_2.	CeO,LaO,DiO.	YO.
5·82	29·08	13·36	21·25	0·92

FeO.	CaO.	Na_2O.	Total.
0·44	23·26	8·98	103·11

Formula $2R''R^{IV}O_3 + NaF$, in which R″ is Ce, La, Di, Y, Fe, Ca, Na_2, and R^{IV} is Si and Ti.

Polylithionite (lithium mica).—Analysis gave—

F.	SiO_2.	Al_2O_3.	FeO.	K_2O.	Na_2O.	Li_2O.	Total.
7·32	59·25	12·07	0·93	5·37	7·63	9·04	101·61*

B. H. B.

Minerals of Litchfield, Maine. By F. W. Clarke (*Amer. J. Sci.*, **31**, 262—272).—The author has examined a number of minerals from boulders of an elæolite rock, in Kennebec Co., Maine.

Elæolite occurs abundantly in Litchfield and West Gardiner in characteristic, dark grey, cleavable masses of strong greasy lustre. Analysis gave the following results:—

H_2O.	SiO_2.	Al_2O_3.	K_2O.	Na_2O.	CaO.	MgO.	Total.
0·86	43·74	34·48	4·55	16·62	trace	trace	100·25

Cancrinite.—The author has analysed three typical samples: A, bright, orange-yellow; B, dirty yellow; and C, bright yellow, granular, the commonest variety. The results were—

	SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	MgO.	H_2O.	CO_2.	Total.
A.	36·29	30·12	4·27	19·56	0·18	—	2·98	6·96	100·36
B.	35·83	29·45	5·12	19·33	0·09	—	3·79	6·50	100·11
C.	37·22	28·32	4·40	19·43	0·18	0·07	3·86	6·22	99·70

Traces of Mn_2O_3 and Fe_2O_3 were observed in each analysis. An analysis of a fresh-coloured mineral which has been called elæolite and cancrinite indiscriminately, gave on analysis the following results:—

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	H_2O.	CO_2.	Total.
38·93	32·52	2·47	17·02	3·23	2·83	2·95	99·95

These figures indicate that the mineral is a mixture of elæolite and cancrinite, but do not show whether the mixture is mechanical or due to isomorphism. A microscopic examination of the material showed the mineral to be a merely mechanical commingling of the two species in equal proportions.

Sodalite.—Analysis of this mineral of an intense blue colour gave the following results:—

SiO_2.	Al_2O_3.	Na_2O.	K_2O.	Cl.	H_2O.	Deduct O.	Total.
37·33	31·87	24·56	0·10	6·83	1·07	1·54	100·22

Hydronephelite, a New Species.—Intimately associated with the sodalite is a white, massive alteration-product. Two specimens were analysed with the following results:—

H_2O.	SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	Cl.	Total.
13·12	38·90	33·98	0·05	13·21	1·01	trace	100·27
13·30	39·24	33·16	trace	13·07	0·88	—	99·65

These results show that the mineral is a new species, and one belonging to the zeolite family. A microscopic examination showed

* 102·11 in original.

that the zeolite must belong either to the quadratic or hexagonal system. The mode of its occurrence indicates clearly that it has resulted from the zeolitisation of the sodalite, a phenomenon which has been observed in many rocks. With the uniaxial zeolite are intermingled small grains of another secondary mineral, biaxial, and probably belonging to one of the two inclined systems of crystallisation. An analysis of carefully purified material shows that the impurity must have been small in amount, and similar in composition to the new zeolite. The formula of the new mineral is

$$Na_2HAl_3(SiO_4)_3,3H_2O.$$

Lepidomelane.—An analysis gave the following results :—

H_2O.	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.
4·62	32·09	18·52	19·49	14·10	1·42

MgO.	K_2O.	Na_2O.	Total.
1·01	8·12	1·55	100·92

This analysis is noteworthy on account of the very low percentage of silica. B. H. B.

Hornblende containing Manganese and Zinc, from Franklin. By J. H. Kloos (*Jahrb. f. Min.*, 1886, i, Mem., 211—223).—The author recently received, from a dealer in Göttingen, a mineral described as jeffersonite, from Franklin, New Jersey. This consists of an aggregate of crystals developed on one side, all with more or less rounded edges. The faces are rough but lustrous, and their colour is dark green. The crystals are columnar, but shortened in the direction of the axis of symmetry, and the two planes, $\infty P\bar{\infty}$, predominate. Their size varies from 10 to 27 mm. in the direction of the vertical axis, and from 10 to 35 mm. in that of the clinodiagonal. It is evident that the mineral is not pyroxene, but hornblende. The sp. gr. is 3·352. On boiling with concentrated hydrochloric acid, the powdered hornblende dissolved completely, flocculent silica separating out. Analysis gave the following results :—

SiO_2.	TiO_2.	Al_2O_3.	Cr_2O_3.	Fe_2O_3.	FeO.	MnO.
39·59	1·76	11·20	0·13	5·97	11·31	3·07

ZnO.	MgO.	CaO.	Na_2O.	K_2O.	H_2O.	Total.
0·53	8·42	12·85	3·31	1·95	1·02	101·11

The constitution of the Franklin hornblende does not agree with the analyses of jeffersonite hitherto published. It is true that the jeffersonite analyses differ considerably from one another, especially in the percentages of manganese, zinc, and alumina ; and it is probable that in several cases the mineral analysed was amphibole.

B. H. B.

The Hainstadt Clays. By C. W. Blomstrand (*J. pr. Chem.* [2], **33**, 483—488).—The author criticises the methods of analysis (which he considers more remarkable than the results) employed by Strohecker in examining these clays (this vol., pp. 314 and 424). Results of analyses are given which show that silica, alumina, and iron are

present in much larger quantities than those given by Strohecker, and that the rare metals are entirely absent. N. H. M.

Note.—Schertel (*Ber.*, **19**, 1368) has also examined the clays for rare metals with negative result. N. H. M.

Chemistry of Sea-water. By A. Hamberg (*J. pr. Chem.* [2], **33**, 433—463; compare this vol., p. 322).—An apparatus is described for estimating nitrogen and carbonic anhydride in sea-water; the boiling out of the gases from the water, and the analysis of the gas boiled out are conducted in the same apparatus. The amount of nitrogen in deep sea-water is the same as the amount absorbed by the water at the surface; the amount of oxygen is somewhat diminished by oxidisable substances in the water. The amount of nitrogen present depends not only on the temperature, but also on the percentage of salts dissolved in the water; thus a difference of 0·2 per cent. of salt dissolved corresponds to a difference of about 0·15 to 0·2 c.c. in the amount of nitrogen (per litre).

The formula $N = 19{\cdot}139 - 0{\cdot}4735t + 0{\cdot}0074t^2$ is given for determining the effect of temperature on the amount of nitrogen in pure water; it can only be used for temperatures up to a little above 20°.

The amount of carbonic anhydride dissolved in sea-water varies with the temperatures, a difference of 10° corresponding with 3—6 per cent. of carbonic anhydride. Tornöe (Norwegian North Atlantic Expedition, 1876–78) and Dittmar (Challenger Expedition, **1**, 103) conclude from the fact that the carbonates present in sea-water are not acid carbonates, that the water contains no free carbonic anhydride. Experiments described by the author show that free carbonic anhydride is present in sea-water; the amount of carbonic anhydride increases as the water is diluted. This is explained by the theory of the chemical action of mass. N. H. M.

Organic Chemistry.

Action of Phosphoric Chloride on Hydrocarbons. By A. Colson and H. Gautier (*Compt. rend.*, **102**, 1075—1077).—When durene is heated with an excess of phosphorus pentachloride at 185—195° for 4 or 5 hours, it yields the symmetrical tetrachloro-derivative $C_6H_2(CH_2Cl)_4$ (1 : 2 : 4 : 5), which forms white crystals, melting at 133—137°. If boiled for a long time with water, it loses all its chlorine as hydrogen chloride, but does not yield any organic acid. The chlorine is, therefore, entirely in the side-chains, but is not in the form of the aldehydic group $CHCl_2$.

A small quantity of another product is also obtained intermediate in composition between the tri- and tetra-chloro-derivatives. When boiled with water, it yields a bitter oil, which is most probably durene-glycerol.

If ethylene chloride is heated at 190° for 10 hours with the quantity of phosphorus pentachloride necessary to convert it into the tetrachloro-derivative $C_2H_2Cl_4$, it yields the trichloro-derivative $C_2H_3Cl_3$, with a larger proportion of the derivative $C_2H_2Cl_4$, which boils between 133° and 146°, and is therefore the symmetrical derivative. It is not altered by prolonged boiling with water, but is decomposed in presence of sodium carbonate, or if heated with water at 175°.

The use of phosphorus pentachloride makes it possible to prepare symmetrical chlorine-derivatives in either the fatty or aromatic series without any production of the isomerides which are always formed in the other methods of preparation. C. H. B.

Action of Hydriodic Acid on Isobutylene. By M. Chéchoukoff (*J. Russ. Chem. Soc.*, 1886, 207—215).—Isobutylene prepared by the action of alcoholic potash on isobutyl iodide, was passed into hydriodic acid saturated at 0°. It was found that an absorption of isobutylene only takes place so long as the concentration of the acid is higher than that of the constant hydrate $2HI + 11H_2O$ (b. p. 127°, sp. gr. 1·7). As soon as this limit is reached, the absorption ceases.

Another series of experiments was undertaken with the view of studying the influence of temperature on this reaction. The hydriodic acid used had the sp. gr. 1·75; it was saturated with isobutylene at 0°, 19°, 39°, 52°, 64°, 72°, 81°, 87°, 100°, 108°, and 117°. After this, the density of the layer of aqueous liquid containing the remainder of the acid was determined. It was found that the density (1·7 at 0°, as already stated) gradually diminishes, reaching a minimum in the experiment at 64°, namely 1·42°; it then again rises, the sp. gr. of the acid formed at 117° being 1·69. This is due to the decomposition of butyl iodide by water and formation of trimethylcarbinol, the maximum quantity of which is formed at 64°.

The author then described his method of separating Puchot's butylene into secondary butyl iodide and pure isobutylene (Abstr., 1885, 495). Tertiary butyl iodide is decomposed by water at the ordinary temperature until the constant hydrate of hydriodic acid is formed; therefore the minimum quantity of water necessary to decompose 100 grams of the iodide is 64 grams. A. T.

Preparation of Mercury Fulminate. By C. A. Lobry de Bruyn (*Ber.*, **19**, 1370—1372).—As an improvement on Beckmann's method for the preparation of mercury fulminate (this vol., p. 606) it is suggested that it is preferable to add the mercury solution to the alcohol, instead of the alcohol to the solution. The danger in this part of the operation is thus removed. If the reaction does not commence of itself, it is merely necessary to slightly warm the mixture. The difference in behaviour of the mixture is analogous to that observed in mixing alcohol and nitric acid together. Thus if the alcohol is added to the acid, the mixture is far more unstable than if the acid is added to the alcohol. The difference is to be accounted for by the presence of nitrous acid and lower oxides of nitrogen in the

nitric acid; the alcohol, added to the acid, is thus in the presence of a considerable quantity of nitrous acid, which, under these conditions, oxidises the alcohol. This oxidation, once commenced, proceeds with accelerated violence, whilst the lower oxides of nitrogen effect the oxidation. V. H. V.

Hexylglycerol obtained from Allyl Dimethyl Carbinol. By D. Orloff (*J. Russ. Chem. Soc.*, 1886, 222—235).—Hexylglycerol was prepared by first adding bromine to dimethyl allyl carbinol and then replacing the two bromine-atoms of this dibromhydrin by hydroxyl. To effect this latter part of the reaction, different methods were tried. The acetate of the dibromhydrin was heated with silver acetate in order to obtain a triacetate of hexylglycerol, but this compound could not be distilled without undergoing decomposition into the diacetate of an unsaturated glycol and acetic acid. A better result was obtained by treating the dibromhydrin with baryta-water; after some time a syrupy substance could be separated from the mixture, soluble in water and in alcohol, insoluble in ether; on analysis it was found to be hexylglycerol. Under a pressure of 17 to 18 mm. it distils at 164·5—165·5°, under 78 mm. at 190—192°; the colourless distillate has the sp. gr. 1·0936 at 0°, and from its mode of formation must have the constitution $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CMe_2{\cdot}OH$.

A more rapid and convenient method for preparing the glycerol consists in treating its monochlorhydrin with potash (compare Abstr., 1886, 138). This monochlorhydrin was prepared by adding aqueous hypochlorous acid to allyl dimethyl carbinol, the mixture being cooled. By the action of alcoholic potash on an ethereal solution of the monochlorhydrin, a colourless liquid was obtained, distilling at 171—178°, partly soluble in water and probably containing a glycid formed by the elimination of a molecule of hydrogen chloride from the monochlorhydrin. No constant product could be obtained by adding chlorine to allyl dimethyl carbinol; an attempt to convert the dichlorhydrin into a glycid, by treating it with potash, also failed.

When iodine was introduced by small portions into a flask containing allyl dimethyl carbinol, mercuric oxide and water, an iodhydrin was formed which could be extracted by ether, and after evaporation of the solvent forms a viscous, brownish, non-crystallisable mass.

Finally the behaviour of the new hexylglycerol towards hydriodic acid was studied. Dilute hydriodic acid does not act on it, concentrated fuming acid forms an iodide, for the main part distilling at 140—150° (probably tertiary hexyl iodide, b. p. 142°), and yielding on treatment with alcoholic potash a hydrocarbon and an alcohol. The former when distilled with metallic sodium passes over at 64—67°; this hydrocarbon seems to be identical with dimethylethylethylene (b. p. 65—67°), obtained from tertiary hexyl iodide. A. T.

Mannitol Dichlorhydrin. By Sivoloboff (*J. Russ. Chem. Soc.*, 1886, 135—141).—To prepare mannitol dichlorhydrin, a solution of 1 part of mannitol in 10 parts of fuming hydrochloric acid (sp. gr. 1·19) is heated at 105—107° in sealed tubes during 20 hours. The

brown liquid is evaporated on a water-bath at 40°, when impure crystals of the dichlorhydrin separate. These are purified by repeated crystallisation from water or boiling alcohol, after treatment of the solution with animal charcoal. From water, the compound is obtained in transparent, colourless tables, from alcohol in thin, white plates, with nacreous lustre. The compound is easily soluble in hot alcohol and is not decomposed by prolonged boiling of the solution. 100 parts of the saturated solution in absolute alcohol contain 2·4 parts of the dichlorhydrin at 15°, and 15·5 parts at the boiling temperature.

By the action of sodium amalgam on an aqueous solution of the dichlorhydrin, no reduction takes place; the first product of the reaction is mannitan monochlorhydrin formed by the loss of one molecule of hydrogen chloride; this substance then loses a second molecule of hydrogen chloride and is converted into β-mannid, an anhydride of mannitol. Unsuccessful attempts were made to reduce the dichlorhydrin by zinc and hydrochloric acid, by hydrogen evolved by electrolysis of hydrogen chloride, by boiling with zinc-dust, and by magnesium in presence of water and traces of platinum chloride.

β-Mannid is a solid melting at 119°, easily soluble in alcohol and in water, and insoluble in ether. 100 parts of its aqueous solution, saturated at 15°, contain 60 parts of β-mannid. It is obtained from aqueous solutions in the form of large bright prisms, from alcoholic solutions in long, thin, acicular prisms. Under a pressure of 16 mm., it distils at 206—210° with scarcely any decomposition; at the ordinary pressure, it slowly sublimes at 140°. The substance is dextrorotatory; a 2·55 per cent. aqueous solution at 21° has the rotatory power $[\alpha]_D = 94·05°$. The addition of the elements of water to β-mannid could not be effected; ammoniacal silver solution is easily reduced by the compound; the oxidation of β-mannid by means of platinum-black yields a syrupy acid. A. T.

Acid Fermentation of Glucose. By Boutroux (*Compt. rend.*, **102**, 924—927).—The acid fermentation of glucose takes place under the influence of a micrococcus resembling that to which the author has previously given the name *M. oblongus*. If this ferment is sown in a solution of glucose in yeast-water containing an excess of chalk, and kept at 35°, crystals of the calcium salt of an acid separate, and before long the surface of the liquid is covered with a crystalline crust. If the zymogluconic acid obtained by the action of *M. oblongus* on glucose is mixed with yeast-water and the ferment under the same conditions, it yields the same product. In order to obtain the free acid, the calcium salt is converted into the cadmium salt, which is purified by recrystallisation, and then decomposed by hydrogen sulphide. The free acid is an almost colourless syrup, with a distinctly acid reaction, very soluble in water and alcohol, but only slightly soluble in ether. It is turned brown by a slight elevation of temperature, or by the addition of a slight excess of alkali, especially ammonia.

The calcium, strontium, and cadmium salts are crystallisable, but

show great tendency to form supersaturated solutions; the potassium, sodium, ammonium, and thallium salts have only been obtained in the form of syrups. The calcium salt crystallises in prisms with a rhombic base, which seem to belong to the monoclinic system; it is only slightly soluble in cold water, but dissolves much more readily in boiling water; the hydrochloric acid solution is distinctly lævogyrate. The strontium salt forms microscopic crystals, which seem to be derived from a prism with a rhombic base; it is only slightly soluble in cold water, but is much more soluble in boiling water. The cadmium salt forms very brilliant crystals, which seem to belong to the monoclinic system; it dissolves in about 65 parts of water at 15°, and is very soluble in boiling water. Concentrated solutions of the salt are gradually decomposed by ebullition.

With normal or basic lead acetate, or with bismuth nitrate, solutions of the salts give white amorphous precipitates, soluble in acetic acid. Concentrated solutions also give crystalline precipitates, which form slowly with salts of calcium and strontium, but they give no precipitate with salts of barium, magnesium, cerium, zinc, iron, or copper. The solutions of the acid and its salts have considerable reducing power. They decolorise alkaline potassium permanganate; reduce silver nitrate slowly in the cold, instantly on boiling, and with ammoniacal silver nitrate they form a silver mirror. Boiling solutions also reduce Fehling's solution, mercurous nitrate, bismuth nitrate, and mercuric chloride.

Analysis of the cadmium and calcium salts shows that the acid has the formula $C_6H_{12}O_8$. It is probably not identical with Maumene's hexepic acid, and the author gives to it the name "*oxygluconic acid.*"

Saccharose yields no acid under the same conditions.

C. H. B.

Anilides of Galactose and Lævulose. By V. Sorokine (*J. Russ. Chem. Soc.*, 1886, 129—132).—This paper has already appeared in part (compare this vol., p. 526).—The anilides of galactose and lævulose are easily obtained in crystals; they even separate out directly from the product of the reaction on cooling. Both have the composition $C_{12}H_{17}NO_5$, and exhibit the same properties; they melt in the dry state at about 147°, are partly decomposed, and become brown at this temperature, solidifying to brown, vitreous masses. The anilides are sparingly soluble in cold alcohol, in hot alcohol they dissolve better, but yet not very readily; they dissolve in cold water, giving a neutral solution, which undergoes no decomposition when heated with alkalis. The anilides give most of the reactions of glucoses; they reduce alkaline solutions of copper, mercury, and silver, and react with picric acid and indigo; but to effect these reactions, more prolonged heating is required than with glucose. The work is being continued.

A. T.

Melezitose. By Alekhine (*J. Russ. Chem. Soc.*, 1886, Ref., 87—88).—The author has examined melezitose, obtained from Turkestan manna (Abstr., 1885, 943) with the following results: crystalline anhydrous melezitose, as well as anhydrous melezitose from crystals

containing water of crystallisation, melt at 147—148°. The anhydrous crystalline compound has the sp. gr. = 1·540 at 17·5 (water at 4° = 1); at 17·5° one part dissolves in three parts of water; the specific rotatory power of these solutions is diminished as the concentration increases. The total inversion of melezitose by dilute acids yields dextrose, which was obtained in the crystalline state, and proves to be identical with ordinary dextrose. A compound of melezitose with phenylhydrazine (yellow needles melting at 172°, when it begins to decompose) was prepared; crystalline compounds with chlorides of the alkali metals are not formed. Octacetylmelezitose forms large, translucent, monoclinic crystals, melting at 170°. The benzene solution of this substance (0·6243 gram in 10 c.c.) has at 20° a specific rotatory power $[\alpha]_D = +110·44°$. Melezitose and octacetylmelezitose do not reduce Fehling's solution even at the boiling temperature. A. T.

Combination of Hydrogen Phosphide with Chloral Hydrate. By J. DE GIRARD (*Compt. rend.*, **102**, 1113—1116).—One part of phosphonium iodide dissolves rapidly in an ethereal solution of two parts chloral hydrate, forming a colourless, highly refractive liquid which fumes in the air. When this liquid is evaporated over sulphuric acid, it deposits small brilliant prisms of dichloralphosphine hydrate, $2PH(CCl_3·CH·OH)_2,H_2O$. The crystals melt at 117—119°, and recrystallise on cooling, but if kept at this temperature they gradually lose water, and are converted into dichloral phosphine melting at 142—144°. The same change takes place when the crystals are heated at 100° in a current of dry air. If rapidly heated in a test-tube, the hydrate melts, and then volatilises with evolution of spontaneously inflammable hydrogen phosphide. It is dissolved by a concentrated solution of potassium hydroxide with development of heat and evolution of hydrogen, and yields a red solution which contains chlorine, formic acid, and hypophosphorous acid.

Butylchloral hydrate under similar conditions yields a compound of buttery consistence.

When 18 parts of dichloralphosphine hydrate are dissolved in 20 grams of acetic anhydride, and the liquid heated in a current of dry air at 130—140° to expel the excess of anhydride, a liquid is obtained which after some days deposits crystals of the composition $PH(CCl_3·CH·OAc)_2,H_2O$, or dichloralphosphine hydrate in which the two alcoholic hydrogens have been replaced by acetyl.

The crystals begin to melt at 72°, but gradually decompose, and fusion is not complete until the temperature reaches 130°. They are insoluble in cold water, but dissolve in boiling water, in alcohol, and in ether, and also in concentrated aqueous potash with development of heat and evolution of hydrogen, forming a solution which contains an acetate.

Acetic anhydride and dichloralphosphine yield a compound which does not readily crystallise, but when the dichloralphosphine is dissolved in propionic anhydride, somewhat soft crystals of the compound $CCl_3·CH(OH)·PH·CH(O·COEt)·CCl_3$ are obtained. They are insoluble in cold water, but dissolve in boiling water, in alcohol, and

in ether. They begin to melt at 88°, but gradually decompose, and fusion is not complete until the temperature rises to 150°. They dissolve in concentrated aqueous potash with development of heat and evolution of hydrogen. C. H. B.

Descent of the Series from Myristic Acid to Lauric Acid. By E. Lutz (*Ber.*, **19**, 1433—1441).—This series of reactions was effected by the method worked out by Hofmann, who has previously effected the descent of the series from the amide of nonylic acid down to normal valeramide (Abstr., 1884, 1114).

Myristotridecylcarbamide, $C_{14}H_{27}O{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_{13}H_{27}$, is prepared by mixing finely powdered myristamide with bromine (equimol. prop.), adding 10 per cent. of aqueous soda, and heating on the water-bath. It is readily separated from unaltered myristamide by its very slight solubility in cold alcohol. It crystallises in stellate groups of silky, white needles, and melts at 103°.

Tridecylamine, $NH_2{\cdot}C_{13}H_{27}$, is prepared by distilling the preceding compound with solid potash. It forms a lustrous, white, fatty mass, melts at 27°, and boils at 265° without decomposition, has an alkaline reaction, eagerly absorbs either water or carbonic anhydride, and is readily soluble in alcohol or ether. The *hydrochloride* forms colourless needles. The *platinochloride*, $(C_{13}H_{27}{\cdot}NH_2)_2,H_2PtCl_6$, crystallises in lustrous, yellow lamellæ, and decomposes at 233°.

Tridecylnitrile, $C_{12}H_{25}{\cdot}CN$, is formed by the action of bromine and aqueous soda on tridecylamine. It is a colourless oil of aromatic odour, boils at 275°, and is insoluble in water, but readily soluble in alcohol and ether. When a mixture of the nitrile and concentrated sulphuric acid is allowed to remain for 24 hours, and is then poured into a large quantity of cold water, *tridecylamide*, $C_{12}H_{25}{\cdot}CONH_2$, separates. This crystallises in silky, colourless plates, melts at 98·5°, and is insoluble in water.

By a similar series of changes, this amide was converted into the amide of lauric acid; the following new compounds being formed. *Tridecylduodecylcarbamide*, $C_{12}H_{25}{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_{13}H_{25}O$, melts at 100·5°. *Duodecylamine*, $C_{12}H_{25}{\cdot}NH_2$, melts at 25°, boils at 247—249°; the hydrochloride, $C_{12}H_{27}N,HCl$, crystallises in yellow needles; the platinochloride, $(C_{12}H_{27}N)_2,H_2PtCl_6$, crystallises in yellow scales, and decomposes at 215°. Laurinamide melts at 97° (Krafft gives 102°, Ehrstadt, 110°). A. J. G.

Butter. By E. Duclaux (*Compt. rend.*, **102**, 1022—1024, 1077—1079).—The author has determined the proportions of volatile acids in butters by means of the method of fractional distillation described in 1865 (*Ann. Chim. Phys.*), the butters examined being a series of prize Normandy butters exhibited at the February exhibition in the Palais d'Industrie. The following results were obtained (p. 686).

With the exception of No. 6, in which the proportion of caseïn is abnormally high, the composition of all these butters is remarkably uniform, and this is especially noticeable in the combined amounts of the volatile acids, and the ratio between the two acids. It may be said, therefore, that the constitution of the glycerides of the volatile

	1.	2.	3.	4.	5.	6.	7.	8.
Water	12·40	13·36	12·28	10·72	13·34	11·62	14·00	13·03
Fat	86·71	85·48	86·76	88·30	86·01	86·52	85·31	86·33
Milk-sugar	0·16	0·20	0·17	0·13	0·20	0·30	0·20	0·11
Caseïn and salts	0·73	0·96	0·79	0·85	0·45	1·56	0·49	0·53
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Caproic acid (per cent.)	2·10	2·18	2·17	2·23	2·26	2·00	2·08	2·19
Butyric acid (per cent.)	3·55	3·52	3·53	3·60	3·65	3·38	3·52	3·46
Sum of the acids	5·65	5·70	5·70	5·83	5·91	5·38	5·60	5·65
Ratio	2·1	2·0	2·0	2·0	2·0	2·1	2·1	2·0

acids is identical in all these butters. Further experiments are necessary, however, to ascertain the influence of breed, locality, and season. A sample of butter from the district of the Meuse, derived from an entirely different breed, showed exactly the same ratio between the two volatile acids.

It is generally supposed that the rancidity of butter is due to a butyric fermentation resulting from the action of microbes derived from the air on the albuminoïds present in the butter. Some very old and salt butters imported from Brazil were found, however, to contain caseïn in its original condition, and when the butter was washed the water was free from microbes. The free acid in the butter had, however, increased to 10 or 20 times its original amount. It follows that the rancidity of butter is not due to microbes, but is the result of a spontaneous decomposition of the glycerides analogous to that which Berthelot has observed in the case of other ethereal salts. This decomposition is accelerated by the presence of water and free acid, but is more or less retarded by salt and borax. Of the different ethereal salts present in butter, butyrin is the least stable, caproïn more stable, and the glycerides of the non-volatile acids still more stable.

This spontaneous decomposition is complicated by the action of air, microbes, and light. The action of air and light results in an absorption of oxygen with formation of carbonic anhydride, the quantity of which is always less than that which corresponds with the amount of oxygen absorbed. The products of oxidation are various, but the most important is formic acid. Oxidation, however feeble, first attacks those substances to which the butter owes its flavour and odour. As oxidation progresses, an odour of tallow is developed, this action being especially rapid in direct sunlight.

In addition to the action of air and light, there is the action of microbes, and especially of cryptogamic vegetations which cover the mass of the butter with their loose, almost invisible mycelia. This action accelerates the decomposition of the glycerides, and at the same time brings about the alteration of the nitrogenous compounds present in the butter. If the albuminoïds are present in small quantity, butyric acid is formed, and its presence accelerates the decomposition of the glycerides, more free acid being liberated up to

a certain point, beyond which the acid is only set free in quantity equal to that which is oxidised or evaporates. The butter remains colourless except where it is in contact with mycelial tubes. When the quantity of albuminoïds is large, the mass becomes alkaline, and the fatty matter darkens in colour owing to its gradual conversion into a black resin completely soluble in alcohol and in alkaline solutions. The resin is also formed in sunlight in presence of an alkali. These facts explain the grey or black colour of old cheese.

C. H. B.

Oxidation of Oils. By A. Livache (*Compt. rend.*, **102**, 1167—1170).—The best method of accelerating the drying of oils (Abstr., 1883, 756, and 1884, 532) is to agitate the oil with a mixture of finely divided lead (precipitated on sheets of zinc or iron from solutions of lead salts) and manganese nitrate, then decant and agitate with lead oxide to decompose the manganese salt. When treated in this way, a thin layer of linseed oil dries completely in less than four hours at the ordinary temperature. The absorption of oxygen takes place much more rapidly with drying than with non-drying oils, but after a time the drying oils which have become quite hard begin to lose weight and become somewhat viscous, whilst non-drying oils continued to increase in weight during the two years over which the experiment extended. The absorption of oxygen results in the partial conversion of the insoluble fatty acids into soluble acids. After two years, the composition of the non-drying oils, so far as the acids are concerned, is very similar to that of the drying oils at the end of one year.

C. H. B.

Dibromacrylic Acid. By H. B. Hill (*Ber.*, **19**, 1396—1397).—The author refers to a paper by Stolz (this vol., p. 530) in which the constitution of a substituted acrylic acid is determined by conversion into the known dibromacrylic acid, melting at 86°. It was previously shown that there are two dibromacrylic acids, both of which melt at 85—86°, but differ in their general behaviour (compare *Ber.*, **14**, 1676; *Proc. Amer. Acad.*, **14**, 211).

N. H. M.

Constitution of Dextrose-carboxylic Acid. By H. Kiliani (*Ber.*, **19**, 1128—1130).—In a previous communication (this vol., p. 526) the author stated that by the reduction of dextrose-carboxylic acid he had obtained a heptolactone. This lactone boils between 216° and 230° at 717 mm., but at the same time undergoes partial decomposition so that it could neither be obtained in a pure state, nor could its true boiling point be ascertained. When boiled with baryta-water, it yields a crystalline salt of a hydroxyheptylic acid. The author found that besides this lactone about an equal quantity of normal heptylic acid was produced during the reduction of dextrose-carboxylic acid. He therefore concludes that dextrose-carboxylic acid is undoubtedly a hexahydroxyheptylic acid, and that dextrose cannot have the constitution of a ketone-alcohol.

L. T. T.

Isomerism of Paraffinoïd Carboxylic Acids. By A. Michael (*Ber.*, **19**, 1381—1386).—The determination of the constitution of unsaturated dicarboxylic acids of the fumaric series from their

halogen additive products (Fittig), and the production of anhydrides (Anschutz), does not appear to the author to be altogether satisfactory, inasmuch as some acids do not readily form halogen additive products, and at the high temperature required for the production of anhydrides isomeric transformations might occur. But the aniline reaction proposed by the author (p. 697) is free from these objections, and can be applied in such cases of isomerism. Thus, as both aconitic and itaconic acids give this reaction they belong to the maleic acid type, and can be represented by the constitutional formulæ

$$COOH\cdot CH : C(COOH)\cdot CH_2\cdot COOH \text{ and } CH_2 : C(COOH)\cdot CH_2\cdot COOH$$

respectively. From similar considerations citraconic acid, as obtained by heating hydroxypyrotartaric acid, has the constitution

$$COOH\cdot CMe : CH\cdot COOH,$$

a formula which is in accordance with the behaviour of bromocitraconic acid in the aniline test. The author considers that mesaconic acid should be represented by the same constitutional formula as citraconic acid, the nature of their isomerism being similar to that observed in the cinnamic acids. It is proposed to use the prefix "allo" for the less stable of two such isomerides: thus fumaric acid might be designated allomaleic acid, or the β-trimethylenecarboxylic acid of Conrad and Guthzeit (Abstr., 1884, 992) as alloitaconic acid. The author considers that this hypothesis of alloisomerism is preferable to improbable and baseless hypotheses of relative arrangement of atoms. V. H. V.

Trimethylenedicarboxylic Acid (1, 1). By W. H. Perkin, jun. (*Ber.*, **19**, 1049—1052; compare Trans., 1885, 820).—The author has again tried the action of benzyl chloride on ethyl trimethylenedicarboxylate in the way suggested by Fittig and Marburg (*Ber.*, **18**, 3414), with the same result as before, the greater part of the benzyl chloride being recovered unchanged.

When ethylic methylmalonate is treated with benzyl chloride and sodium, a small quantity of benzyl ether and much ethylic benzylmethylmalonate are formed: Fittig and Marburg (*loc. cit.*) obtained nothing but benzyl ether.

Trimethylenedicarboxylic acid is not acted on by bromine in the dark; in yielding a bromine-derivative in presence of light, it behaves in a manner analogous to trimethylene. A bromine-derivative formed by the splitting of the trimethylene-ring would have the constitution $CBr(COOH)_2\cdot CH_2\cdot CH_2Br$, or $C(COOH)_2\cdot(CH_2Br)_2$, whilst the constitution of a bromine-derivative of a vinylmalonic acid would be $CH(COOH)_2\cdot CHBr\cdot CH_2Br$.

Nitric acid has no action on tri- or tetra-methylenedicarboxylic acid, which, therefore, in this respect behave like disubstituted malonic acids, and unlike the monosubstituted malonic acids (compare Franchimont, Abstr., 1885, 964).

The optical properties of trimethylenedicarboxylic acid, as well as its magnetic circular polarisation, point to its being a saturated compound. N. H. M.

Action of Trimethylene Bromide on Ethylic Sodacetoacetate. By W. H. PERKIN, jun. (*Ber.*, **19**, 1244—1247).—The compound $C_{10}H_{16}O_4$ obtained by the action of trimethylene bromide on ethyl sodiomalonate (Abstr., 1883, 1083) can only be ethylic allylmalonate or tetramethylenedicarboxylate; on the other hand, the product of the reaction between trimethylene bromide and ethylic sodacetoacetate could be formed in a manner analogous to either of those compounds, or the ketonic oxygen of the ethylic acetoacetate could take part in the reaction with formation of a compound

$$COOEt\cdot C\lessdot\begin{matrix}CMe—O\\CH_2\cdot CH_2\end{matrix}\gtrdot CH_2.$$

This latter view is probably correct, as the magnetic rotation of ethylic acetyltetramethylenecarboxylate excludes the possibility of its being a tetramethylene-derivative; it would also account for the fact that the compound does not react with phenylhydrazine.

Ethylic acetyltrimethylenecarboxylate appears to have the constitution previously assigned to it (Trans., 1885, 829); it reacts readily with phenylhydrazine, and its physical properties show that its constitution is similar to that of ethylic trimethylenecarboxylate.

N. H. M.

Isosaccharic Acid. By F. TIEMANN and R. HAARMANN (*Ber.*, **19**, 1257—1281; compare Abstr., 1884, 724).—The specific rotation of isosaccharic acid is 46·12; it is not affected by heating the substance at high temperatures. The *ammonium salt*, $C_6H_8(NH_4)_2O_8$, crystallises in needles; the *lead salt* (with 2 mols. H_2O) also forms needles. The ethyl salt (*loc. cit.*) boils without decomposition in a current of carbonic anhydride at 250° (uncorr.); its specific rotation = 35·5.

The *esoanhydride of isosaccharic diamide*, $C_4H_4O(OH)_2(CONH_2)_2$, is obtained by dissolving ethyl isosaccharate in alcoholic ammonia; after some hours crystals separate. It melts at 226° and is readily soluble in water, sparingly in alcohol and ether; the specific rotation is 7·16. When boiled with aqueous hydrochloric acid, it is converted into isosaccharic acid.

The *esoanhydride of isosaccharic dianilide*, $C_4H_4O(OH)_2(CO\cdot NHPh)_2$, is prepared by heating ethyl isosaccharate for three to four hours with sufficient aniline to dissolve it. When cold, the product forms a thick syrup which deposits crystals if treated with ether. It crystallises in white needles sparingly soluble in water, readily in alcohol, ether, benzene, &c.; it melts at 231°.

When 5 grams of isosaccharic acid is heated with 50 grams of hydriodic acid (sp. gr. = 1·67) and 2 grams of amorphous phosphorus at 145—150°, adipic acid is formed. The carbon-atoms in isosaccharic acid must therefore form a chain.

Ethyl tetracetylisosaccharate, $C_4H_4(OAc)_4(COOEt)_2$, is obtained by heating ethyl isosaccharate with acetic chloride at 100° for one hour. It forms white needles readily soluble in water, alcohol, and ether, &c.; it melts at 47°. When exposed to air, it is gradually decomposed with liberation of acetic acid. The formation of this tetracetyl-

derivative shows that isosaccharic acid is normal tetrahydroxyadipic acid, $COOH\cdot[CH(OH)]_4\cdot COOH$.

Tetracetylisosaccharic acid, $C_{14}H_{18}O_{12}$, is prepared by digesting isosaccharic acid with an excess of acetic chloride for several hours at 100°. It crystallises in needles (with 1 mol. H_2O) melting at 101°.

It was previously shown (*loc. cit.*) that isosaccharic acid decomposes when heated with formation of pyromucic acid. When heated in a stream of dry hydrogen chloride, it yields dehydromucic acid. Assuming furfurane, the basis of pyromucic acid, to have the constitution $<^{CH:CH}_{CH:CH}>O$, a furfuranedicarboxylic acid derived from normal tetrahydroxyadipic acid must have the constitution

$$<^{CH:C(COOH)}_{CH:C(COOH)}>O;$$

dehydromucic acid is therefore furfurane-$\alpha\alpha'$-dicarboxylic acid.

Hydrochlorofurfurane-$\alpha\alpha'$-dicarboxylic acid, $C_4H_3ClO(COOH)_2$, is obtained by heating isosaccharic acid (1 mol.) with phosphorus pentachloride (6 mols.) for 50 hours, by which time the evolution of hydrogen chloride ceases. The product is distilled until the temperature in the retort is a little above 110°, and the residue treated gradually with a concentrated solution of sodium carbonate; it is then warmed slightly, diluted with water, treated with sulphuric acid, and extracted with ether. It forms long, white needles, melting above 340°, soluble in water, alcohol, and ether, insoluble in chloroform, benzene, &c. The *barium*, *calcium*, and *silver* salts were prepared; the *ethyl salt* crystallises in white needles melting at 40°; it is readily soluble in the usual solvents. When hydrochlorofurfuranedicarboxylic acid is boiled with a solution of potash, it gives up the elements of hydrochloric acid and yields potassium furfurane-$\alpha\alpha'$-dicarboxylate.

The esoanhydride of isosaccharic diamide decomposes, when distilled in a stream of carbonic anhydride, yielding as chief product pyromucamide; a trace of pyrroline or of a derivative of pyrroline is formed. The same product was obtained by distilling ammonium isosaccharate. These results make it probable that the internal anhydrides of isosaccharic diamide and dianilide are hydroxyl-derivatives of tetrahydroxylfurfuranedicarboxylic amide and anilide respectively; their constitution would be expressed by the formulæ:—

$$<^{CH(OH)\cdot CH(CO\cdot NH_2)}_{CH(OH)\cdot CH(CO\cdot NH_2)}>O \text{ and } <^{CH(OH)\cdot CH(CO\cdot NHPh)}_{CH(OH)\cdot CH(CO\cdot NHPh)}>O.$$

When isosaccharic acid is distilled with phosphorus pentasulphide, a distillate is obtained which gives a distinct indophenine reaction with sulphuric acid and isatin; no thiophen or thiophen-derivative could, however, be isolated. By heating isosaccharic acid with barium sulphide at 210° for six hours, a product is obtained four-fifths of which consists of pyromucic acid and one-fifth of thiophencarboxylic acid. N. H. M.

Condensation of Formaldehyde with Ethyl Malonate. By W. H. PERKIN, jun. (*Ber.*, **19**, 1053—1057).—*Ethyl propanetetracarboxylate*, $CH(COOEt)_2 \cdot CH_2 \cdot CH(COOEt)_2$, is prepared by the method of Claisen and Komnenos (*Annalen*, **218**, 145) by heating 30 grams of ethyl malonate, 5 grams of paraformaldehyde, and 45 grams of acetic anhydride for two days at 120—140°. It is then distilled, and the residue boiling above 250°, which forms the greater part of the product of the reaction, fractionated in a vacuum. It is a very thick, colourless oil having a slight odour, and boils at 240—241° under 100 mm. pressure; when pure, it boils at the ordinary pressure with scarcely any decomposition. When saponified with alcoholic potash, a thick oily acid is obtained which on heating at 200—220° gives off carbonic anhydride with formation of glutaric acid.

When sodium ethoxide (2 mols.) is added to an ethereal solution of ethyl propanetetracarboxylate, a *compound* $C_{15}H_{22}Na_2O_8$, separates as a thick voluminous precipitate. This was treated with bromine and the product of the reaction treated with water and extracted with ether. The oil obtained by evaporating the ether was then saponified with alcoholic potash. The free acid obtained from the potassium salt was heated at 180—200°, when it decomposed with evolution of carbonic anhydride, yielding an acid having the properties of trimethylenedicarboxylic acid (1, 2); the yield of acid was too small to completely establish the identity. N. H. M.

Action of Alcoholic Potash on Carbamide, Thiocarbamide, and Substituted Carbamides. By A. HALLER (*Compt. rend.*, **102**, 974—976).—2—2·5 grams of the carbamide was heated in sealed tubes with an equivalent quantity of potassium hydroxide and 20 grams of absolute alcohol. Carbamide yields potassium cyanate, ammonia, and water, in accordance with the equation $CO(NH_2)_2 + KHO = KCNO + NH_3 + H_2O$. Monethylcarbamide yields potassium cyanate and ethylamine, and non-symmetrical diethylcarbamide yields potassium cyanate and diethylamine. Thiocarbamide and ammonium thiocyanate can be converted into one another by heating to 160—170°, but if thiocarbamide is heated with alcoholic potash the conversion begins below 100°. When the mixture is heated at 100° for several hours, the reaction is more complicated; potassium thiocyanate and ammonium sulphide are formed, whilst a large proportion of the thiocarbamide remains unaltered.

Ethyl isocyanate and isocyanurate yield with alcoholic potash the same products as with aqueous potash; namely, potassium carbonate and ethylamine.

These results show that carbamide and the substituted carbamides of the formulæ CON_2H_3R and $NH_2 \cdot CONR_2$ in presence of alcohol undergo the inverse change to that by which their synthesis is effected. This fact to a certain extent supports the constitutional formula for urea proposed by Gautier, $CO : N \cdot NH_4$, but although this formula enables the constitution of the monoalkyl ureas, and the non-symmetrical dialkyl ureas to be represented, it admits of no representation of the constitution of the symmetrical dialkyl-derivatives.

C. H. B.

Urethanes of the Paraffin Series. By G. Arth (*Compt. rend.*, **102**, 977—978).—Isobutyl, amyl, and capryl carbamates, like ethyl carbamate, when heated with equivalent quantities of alcoholic potash, yield potassium cyanate and the corresponding alcohols. It follows therefore that carbamates of the paraffin series in contact with alcoholic potash decompose in accordance with the general equation $NH_2{\cdot}CO{\cdot}OC_nH_{2n+1} + KOH = KCNO + H_2O + C_nH_{2n+1}{\cdot}OH$, and in this respect resemble camphor and menthol carbamates.

Octyl carbamate can be prepared by the usual reaction, boils at 135° under a pressure of 20 mm., and crystallises easily. It is insoluble in cold water and almost insoluble in boiling water, but dissolves very easily in alcohol, from which it separates in colourless crystals melting at 54—55°. When heated under ordinary pressure, it boils at 230—232°, and is at the same time partially converted into cyanuric acid. In this respect it differs from the lower members of the same series, but resembles the carbamates of camphor and menthol. C. H. B.

Benzene containing Thiophen. By C. Willgerodt (*J. pr. Chem.* [2], **33**, 479—483).—The following lecture experiments show the removal of thiophen from benzene: (1) Chlorine is passed into 50 grams of benzene for 10 to 15 minutes; hydrochloric acid is given off. The product is distilled and the distillate treated with caustic soda to remove the halogen; it then no longer gives the indophenine reaction. (2) 10 c.c. of benzene are shaken with freshly prepared chlorine-water for 10 minutes; the coloured benzene is then poured off, treated with soda, and tested for thiophen which is found to be absent. (3) The same result is obtained by adding bromine to benzene until the latter has a distinctly yellow colour, and then distilling off the benzene and treating the distillate as already described. (4) 5 c.c. of the purified benzene are treated with chlorine or bromine; on adding a drop of thiophen the liquid fumes from evolution of hydrochloric or hydrobromic acid. It is best to use bromine and to heat the benzene to its boiling point after the addition of thiophen.

In order to purify a large quantity of benzene from thiophen, chlorine was passed for four hours through 4 kilos. of benzene cooled with ice and kept in the dark. The greater part then distilled at 50—85°, and was found to be free from thiophen. N. H. M.

Ethyl Phenylthioformate (Ethyl Phenylthiocarbonate). By R. Otto and A. Rössing (*Ber.*, **19**, 1227—1234).—Ethylic phenylthioformate, SPh·COOEt (Abstr., 1885, 1231), is prepared by boiling zinc phenylmercaptide (obtained by the action of zinc-dust on thiophenol dissolved in absolute alcohol) with ethyl chlorocarbonate (2 mols.) dissolved in benzene until the odour of the latter has disappeared. More ethyl chlorocarbonate is added and the boiling continued; the clear benzene solution is then poured off and distilled. The fraction boiling at 220—270° contains the ethyl phenylthioformate; this is a very refractive yellowish liquid, having a disagreeable odour, insoluble in water, miscible with ether and alcohol

in all proportions. Thiophenol and ethylphenyl sulphide are formed in the reaction. When ethyl phenylthioformate is heated with a 25 per cent. solution of soda it is decomposed into ethylphenyl sulphide, together with some phenyl hydrogen sulphide and ethyl alcohol. The same result was obtained by the action of water at 230°. Ethylic ethylthioformate behaves in a similar manner; ethyl sulphide is formed, but only in small quantities, the chief products being alcohol and ethyl hydrogen sulphide (compare this Journal, 1873, 617). Alcoholic ammonia acts on ethyl phenylthioformate yielding urethane, thiophenol, carbamide, and ethyl phenyl sulphide. Potassium permanganate oxidises ethyl phenylthioformate with formation of potassium benzenesulphonate. N. H. M.

Dinitrophenyl Thiocyanate. By P. T. Austin and F. S. Smith (*Amer. Chem. J.*, **8**, 89—92).—*Dinitrophenyl thiocyanate*, $C_6H_3(NO_2)_2{\cdot}SCN$.—Dinitrobrombenzene was boiled in alcoholic solution with potassium thiocyanate so long as a yellow, crystalline powder separated; this substance is purified by treatment with methyl alcohol and water; it melts at 139°. When heated with concentrated sulphuric acid, it is converted into *dinitrophenyl mercaptan*, $C_6H_3(NO_2)_2{\cdot}SH$, a light yellow powder, insoluble in the usual solvents; it melts at 195°. *Dinitrophenyl sulphide*, $S(C_6H_3N_2O_4)_2$, is formed by treating the dinitrophenyl thiocyanate with strong nitric and sulphuric acids. It crystallises well from glacial acetic acid, the crystals melt at 245°; another dinitrophenyl sulphide has been described by Beilstein and Kurbatow (Abstr., 1879, 230). H. B.

Phenylnitromethane. By S. Gabriel and M. Koppe (*Ber.*, **19**, 1145—1148).—If phenylnitromethane (Abstr., 1885, 902) is heated with fuming hydrochloric acid at 150°, it is decomposed into benzoic acid and hydroxylamine. When treated with alcoholic soda, it forms a crystalline magma probably containing the sodium-derivative. When bromine acts on an aqueous solution of the sodium-derivative of nitrobenzylidenephthalide, *phenyldibromonitromethane*, $CPhBr_2{\cdot}NO_2$, is formed. This is a colourless liquid of pungent odour. When iodine is substituted for bromine in the above reaction, a compound, C_7H_5NO, is obtained which is identical with the substance obtained by Koreff from diphenylglyoxime (this vol., p. 363). Koreff ascribes to his compound the formula $<\begin{matrix}CPh:NO\\CPh:NO\end{matrix}>$. The vapour-density, as determined in V. Meyer's apparatus, corresponded with the simple formula C_7H_5NO; but as the substance used in the determination was found after the conclusion of the experiment to have been entirely converted into phenyl cyanate, the vapour-density is probably not that of the original substance. From its mode of formation, the author was inclined to ascribe to this compound the formula CPh : N : O or $CPh<\begin{matrix}N\\O\end{matrix}>$, but either of these compounds should be broken up by hydrochloric acid into benzoic acid and hydroxylamine, whilst the compound in question is unacted on by hydrochloric acid even at 200°. L. T. T.

Action of Chromyl Chloride on Nitrotoluene. By V. v. Richter (*Ber.*, **19**, 1060—1062).—Etard (Abstr., 1881, 581) has already tried the action of chromyl chloride on ordinary nitrotoluene, and obtained a compound, $NO_2 \cdot C_7H_8O_2$, which he described as nitrotoluquinone. The author, however, obtained from paranitrotoluene and chromyl chloride an almost theoretical amount of paranitrobenzaldehyde:—45 grams of chromyl chloride were added to a solution of 20 grams of paranitrotoluene in 80—100 grams of carbon bisulphide. After some days, a compound of paranitrotoluene with chromylic chloride, $NO_2 \cdot C_6H_4Me, 2CrO_2Cl_2$, separates as a dark-brown powder. This is filtered, washed with carbon bisulphide, and then put into water, when it decomposes with formation of chromium salts and paranitrobenzaldehyde. This is crystallised from water or purified by means of the hydrogen sodium sulphite compound.

Orthonitrotoluene also forms a compound with chromylic chloride, which, however, yields only a small quantity of orthonitrobenzaldehyde when treated with water, the greater part being decomposed into its constituents.

The compound obtained by Etard (*loc. cit.*) at a temperature of 150—170° is probably paranitrobenzoic acid. N. H. M.

Action of Sulphuric Acid on Durene; the Third Tetramethylbenzene. By O. Jacobsen (*Ber.*, **19**, 1209—1217; compare this vol., p. 67).—When durene is kept in contact with 10 times its weight of sulphuric acid for 6—8 hours, the whole being frequently shaken, about one-quarter goes into solution, and by the addition of ice a crystalline sulphonic acid can be separated and was identified as durenesulphonic acid. When the latter is shaken with cold sulphuric acid, a separation of durene takes place.

Pure dry sodium durenesulphonate was frequently shaken with sulphuric acid (sp. gr. = 1·839) during four days, and then heated for 12 hours at 40—50°. It was then treated with ice, and the sulphonic acid so obtained dissolved in water; the solution was extracted with light petroleum, which on evaporation yielded a hydrocarbon having all the properties of hexamethylbenzene. The mixed sulphonic acids yielded three amides: the most sparingly soluble amide forms lustrous prisms melting at 187°; the second amide crystallises in needles which melt at 170—172°; and the third resembles metaxylylsulphonamide; its melting point varies between 110° and 116°.

Prehnitene (consecutive tetramethylbenzene), $C_6H_2Me_4$, is obtained by heating the amide melting at 187° with hydrochloric acid at 170—180°; it boils at 204°, and when cooled solidifies to a crystalline mass which melts at − 4°. When treated with an excess of bromine in presence of iodine, *dibromoprehnitene*, $C_{10}H_{12}Br_2$, is formed. This crystallises in long, colourless prisms, readily soluble in toluene, sparingly soluble in alcohol; it melts at 210°. *Dinitroprehnitene*, $C_{10}H_{12}(NO_2)_2$, is formed by the action of cold nitric and sulphuric acids (mixed) on the hydrocarbon; it crystallises from alcohol in yellowish-white prisms, having a glassy lustre, and melts at 178°.

Prehnitenesulphonic acid, $C_{10}H_{13} \cdot SO_3H$, is prepared by dissolving the hydrocarbon in warm sulphuric acid. It forms small needles with

water of crystallisation. The *barium salt* forms small flat crystals sparingly soluble in hot water; the *sodium salt* (with 1 mol. H_2O) crystallises in small, lustrous plates, readily soluble in water.

Prehnitylic acid, $C_6H_2Me_3{\cdot}COOH$ [= 1 : 2 : 3 : 4], is obtained by boiling prehnitene with nitric acid (sp. gr. = 1·4), diluted with four parts of water, for 12 hours. It forms very long transparent prisms with a glassy lustre, melting at 167·5°; it is readily soluble in hot alcohol, and can be distilled without decomposition. The *calcium salt* (with 4 mols. H_2O ?) crystallises in flat transparent prisms moderately soluble in water. When distilled with an excess of lime, it yields hemellithene.

The two amides already mentioned, melting at 170—172° and at 110—116°, when heated with hydrochloric acid at 170—180°, yield pseudocumene, and are therefore derivatives of 1 : 3 : 4 : 5 and 1 : 3 : 4 : 2 pseudocumenesulphonic acids.

Pentamethylbenzene is more quickly acted on by sulphuric acid than is durene; the products are isodurene, and a solid crystalline hydrocarbon which melts at 165°. The latter is, perhaps, octomethylanthracene.

Schulze (this vol., p. 232) extracted durene by means of fuming sulphuric acid, and recovered the hydrocarbon by distilling with steam; in this case a disulphonic acid is formed which is much more stable than the monosulphonic acid obtained by the action of cold sulphuric acid on durene.

Durenedisulphonamide, $C_{10}H_{12}(SO_2{\cdot}NH_2)_2$, crystallises in well-formed microscopic crystals, which melt above 310°; it is sparingly soluble in water. N. H. M.

Reaction between Aldehydes and Phenol. By A. Michael and J. P. Ryder (*Ber.*, **19**, 1388—1390).—According to Baeyer (this Journal, 1872, 301) the resin, as also the crystalline compound obtained by the reaction between benzaldehyde and resorcinol, has the composition $C_{26}H_{20}O_4$, whilst that from pyrogallol has the composition $C_{26}H_{22}O_7$, although analogy would point to a formula $C_{26}H_{20}O_6$. By repetition of the experiments, the latter formula has been confirmed, and from the compound an *acetyl-derivative*, $C_{26}H_{14}O_6Ac_6$, has been obtained in the form of prismatic crystals. By heating aqueous solutions of chloral hydrate and resorcinol, a compound probably of the composition $C_8H_6O_3$ is produced, but from its ready oxidisability it could not be obtained in the pure state. Orcinol under the same conditions yields a substance crystallising in needles of the composition $C_{23}H_{24}O_8$, formed thus: $3C_6H_3Me(OH)_2 + CCl_3{\cdot}CH(OH)_2 = [C_6H_2Me(OH)_2]_3C{\cdot}CH(OH)_2 + 3HCl$. With acetic anhydride, it gives a hexacetyl-derivative which melts at 185°. V. H. V.

Formation of Quinol. By G. Ciamician (*Gazzetta*, **16**, 111—112).—When an alcoholic solution of quinone is exposed to bright sunlight for a few days it yields quinol and ethaldehyde, thus: $C_6H_4O_2 + C_2H_6O = C_6H_6O_2 + C_2H_4O_2$. At present, the author is unable to state whether light is necessary for the production of this change. V. H. V.

Quinol-derivatives of the Benzene Series. By P. DE CLERMONT and P. CHAUTARD (*Compt. rend.*, **102**, 1072—1075).—When quinone is brought into contact with a large excess of acetic chloride, hydrogen chloride is evolved, heat is developed, and the quinone is completely decolorised. The products are phenyl acetate and chloracetylquinol, $OH{\cdot}C_6H_3Cl{\cdot}OAc$, which forms silky tufts, or beautiful transparent, rectangular prisms melting at 60°. Benzoic chloride and acetic bromide under similar conditions yield analogous compounds.

Catechoquinone, $OH{\cdot}C_6H_4{\cdot}O{\cdot}O{\cdot}C_6H_4{\cdot}OH$, is easily obtained by mixing ethereal solutions of quinone and catechol in equivalent proportions. It crystallises in deep green needles with a metallic lustre, which melt at 153°, and sublime with decomposition at a higher temperature. It is readily affected by acids and alkalis, and is converted into a mixture of catechol and quinol by a current of sulphurous anhydride. Like its isomerides, quinhydrone and resorquinone, it is readily decomposed by alcoholic chlorides, with formation of the corresponding phenol and ethereal derivatives of quinol.

Pyrogalloquinone, obtained by the direct action of pyrogallol on quinone (Wichelhaus), is identical with the purpurogallin obtained by the oxidation of pyrogallol. Both substances give the same reactions, and both yield a tetracetyl-derivative. Pyrogalloquinone differs from the other phenoquinones in both its chemical and physical properties. It is not affected by alcoholic chlorides, and is characterised by very much greater stability. It probably has the constitution $C_{10}H_6(OH)_2{\cdot}O_2{\cdot}O{\cdot}O_2C_{10}H_6(OH)_2$.

Phloroquinone is obtained by mixing ethereal solutions of phloroglucol (2 mols.) and quinone (1 mol.). It forms rectangular tables, which are red by transmitted light but green with a metallic lustre by reflected light. It does not sublime without decomposition, is decomposed by acids and alkalis, and is converted into phloroglucol and quinol by sulphurous anhydride. When phloroglucol and quinone are mixed, there is no evolution of gas as in the case of pyrogallol, and in all respects phloroquinone resembles the other phenoquinones much more closely than pyrogalloquinone. C. H. B.

Metaisocymophenol. By J. A. JESURUN (*Ber.*, **19**, 1413—1417).—Metaisocymene (1.3 methylpropylbenzene) was prepared from resin oil by Kelbe (Abstr., 1882, 299), who obtained amongst other derivatives the phenol, cymenol. The present paper deals with the derivatives of this phenol.

Cymenyl methyl ether, $C_6H_3MePr{\cdot}OMe$ [2 : 4 : 1], prepared by heating cymenol with excess of methyl iodide and a solution of potash in methyl alcohol at 100—120°, is an oil of aromatic odour and burning taste which boils at 217°. When treated with nitric and sulphuric acids, it yields a *mononitro*-derivative as an orange-red oil. *Cymenyl ethyl ether*, $C_6H_3MePr{\cdot}OEt$, is an oil of aromatic odour boiling at 224°.

Cymenotic acid, $OH{\cdot}C_6H_2MePr{\cdot}COOH$, isomeric with thymotic and carvacrotic acids, is obtained by the action of sodium and carbonic anhydride on cymenol. It crystallises in long, slender needles, melts

at 147°, is sparingly soluble in hot water, readily soluble in alcohol, and gives a bluish-violet coloration with ferric chloride. When heated with hydrochloric acid in sealed tubes, it is resolved into cymenol and carbonic anhydride. The last two reactions point to the ortho-position of the hydroxyl and carboxyl groups, the acid therefore has the constitution [OH : Me : Pr : COOH = 1 : 2 : 4 : 6]. The silver and barium salts are described. The *methyl* salt crystallises in short needles, and melts at 148°.

Tribromocymenol, $C_6Br_3MePr{\cdot}OH$, is prepared by agitating an aqueous solution of cymenol with a solution of bromine in hydrobromic acid. It crystallises in plates of golden lustre, which turn brown at 215°, and melt at 221—222° with decomposition.

The constitution [OH : Me : Pr = 1 : 2 : 4] assigned to cymenol is proved by gently fusing it with potash, when it yields α-hydroxyisophthalic acid (prepared by Jacobsen from 1 . 3 . 4 metaxylenol) and cumophenolcarboxylic acid (prepared by Paterno and Mazzara by the action of carbonic anhydride and sodium on paracumophenol). The nature of the propyl-group cannot yet be decided. A. J. G.

Constitution of Safrole. By T. Poleck (*Ber.*, **19**, 1094—1098).—In consequence of Eijkman's work on this subject (this vol., p. 95), the author has repeated Schiff's experiments (Abstr., 1884, 1338). He succeeded in obtaining piperonic acid, and otherwise fully confirms Eijkman's results. After discussing the various data available, he adopts Eijkman's formula, $C_3H_5{\cdot}C_6H_3(OH){\cdot}OMe$, in place of that proposed by himself (Abstr., 1884, 1339). L. T. T.

Citraconic Acid as a Reagent for Aromatic Amines. By A. Michael (*Ber.*, **19**, 1390—1392).—When an aqueous solution of a primary aromatic amine is heated with an equimolecular proportion of citraconic acid, an insoluble anilide is produced, whilst the secondary and tertiary amines under like conditions give no precipitate, but volatilise with the vapour of water. It is here proposed to found on this difference of behaviour a method for the recognition and separation of the primary from the secondary and tertiary amines.

The mixture of the bases is dissolved in an aqueous solution of citraconic acid, an equal quantity of the acid added, and the mixture heated in a reflux apparatus so long as a precipitate forms. The filtrate from this precipitate is distilled to collect the unaltered amines.

It is further noticed that from a clear solution of aniline acetate, aniline separates out on heating, then a neutral solution is produced, and finally acetic acid is left. But methylaniline and ethylaniline do not undergo these changes. It is thus possible to make this property also a method for the indication and separation of the primary amines from their isomerides. V. H. V.

Formation of Anilides and Constitution of Polybasic Unsaturated Acids. By A. Michael (*Ber.*, **19**, 1372—1375).—Gottlieb (*Annalen*, **77**, 277) has observed that an aqueous solution of aniline mesaconate undergoes no change when heated, whilst aniline citr-

aconate is decomposed under the same conditions with formation of phenyl citraconimide. Similarly, on heating an aqueous solution of aniline maleate, white needles of the anilide $C_2H_2(CONHPh)_2$, melting at 211°, separate, whilst a compound, more soluble in alcohol and insoluble in alkalis, is simultaneously formed; probably the phenylimide. Fumaric acid treated in the same way remains unaltered. This difference in behaviour with aniline is common to all derivatives of maleic and fumaric acids respectively. It is thus possible to determine, even with small quantities of substance, whether an acid belongs to one or other of the above series. For example, aconitic and acetylenedicarboxylic acids give the reaction, although in the latter case it is complicated by subsidiary changes.

V. H. V.

Formation of Anilides. By A. Michael and G. M. Palmer (*Ber.* **19**, 1375—1376).—On adding an aqueous solution of maleic acid to a sufficient quantity of aniline, phenylmaleamic acid, $COOH{\cdot}C_2H_2{\cdot}CONHPh$, is produced; it crystallises in prisms which melt at 207°. Citraconic acid forms with aniline a phenylimide, melting at 98°, slowly converted, when in solution, into citraconanilic acid, which crystallises in large rhombic prisms or needles and melts at 175°. A similar result is obtained with itaconic acid. As regards the reaction with aniline, phthalic acid is differentiated from its isomerides, inasmuch as the former yields a crystalline phthalylphenylimide, melting at 205°, whilst the latter are unaltered. V. H. V.

Action of Aniline on Bromomaleic and Chlorofumaric Acid. By A. Michael (*Ber.*, **19**, 1377—1378).—By heating aniline hydrogen bromomaleate, or by treatment of bromo- or chloro-fumaric acid with aniline, two compounds are formed, namely, the phenylimide of phenylamidomaleic acid, $NHPh{\cdot}C\lessgtr^{-CO-}_{CH{\cdot}CO}\gtrNPh$, and the acid anilide of the same acid, $NHPh{\cdot}CO{\cdot}C(NHPh) : CH{\cdot}COOH$, of which the latter is soluble, the former insoluble in water. The former crystallises in minute, yellow needles which melt at 230°; the latter melts at 176°, and has acid properties. These reactions offer an interesting example of the conversion of derivatives of fumaric into those of maleic acid at the temperature of boiling water; a similar example of such an isomeric transformation has been observed by Friedrich in the production of β-ethoxycrotonic from β-chlorisotonic acid.

V. H. V.

Amidobenzylamine. By H. Amsel and A. W. Hofmann (*Ber.*, **19**, 1284—1290).—Benzylacetamide is prepared by boiling benzylamine with an excess of glacial acetic acid for three hours. It melts at 60—61° (Strakosch, this Journal, 1874, 78, ascribed to it the melting point 36°, and Rudolph, Abstr., 1879, 921, 59°) and boils above 300°. It dissolves in water, light petroleum, alcohol, and ether. When added to well cooled, fuming nitric acid, *paranitrobenzylacetamide* is obtained. This forms almost white needles soluble in alcohol, less soluble in ether and benzene; it melts at 125°. When oxidised, it yields paranitrobenzoic acid.

Amidobenzylamine, $NH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}NH_2$, is obtained by the action of

tin and hydrochloric acid on the nitro-compound. It forms an almost colourless oil boiling at 268—270°, sp. gr. = 1·08 at 20°. It has decided basic properties, and very readily absorbs carbonic anhydride from the air. It is soluble in water and alcohol, insoluble in ether. The *hydrochloride* forms a crystalline substance readily soluble in water, almost insoluble in absolute alcohol and insoluble in ether. The *platinochloride* and *stannochloride* were prepared. The *carbamide* of *amidobenzylamine* $NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH_2$, is prepared by heating the hydrochloride of the base (1 mol.) with potassium cyanate (2 mols.) at 100°; it crystallises from water in groups of small needles which melt at 197° with decomposition. The corresponding *thiocarbamide* is prepared in a similar manner; it forms white needles melting at 176°.

Amidobenzylamine reacts with carbon bisulphide with formation of a compound melting at 139°. N. H. M.

Separation of Xylidines. By O. N. Witt (*Dingl. polyt. J.*, **260**, 95).—Commercial xylidine consists of about 75 per cent. of amidometaxylidine and 25 per cent. of amidoparaxylidine. The author has found that by the difference in the solubility of the monosulphonic acids of these bases their separation can be effected without difficulty. The metaxylidinemonosulphonic acid is nearly insoluble in water and dilute acids, and its sodium salt is freely soluble. Paraxylidinesulphonic acid is readily soluble, and forms a sodium salt which crystallises in pearly scales sparingly soluble in water. D. B.

Nitration of Phenylhydrazine. By A. Michael (*Ber.*, **19**, 1386—1388).—As experiments on the direct nitration of phenylhydrazine have hitherto proved unsuccessful, the author in this paper gives an account of some preliminary experiments made to effect the change by indirect processes. Acetophenylcitraconazide, obtained by boiling aqueous solutions of phenylhydrazine and citraconic acid, is dissolved in concentrated sulphuric acid, and to the solution is slowly added a well-cooled mixture of equal volumes of fuming nitric and sulphuric acids; a mononitro-derivative, $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}Ac : C_2O_2C_3H_4$, crystallising in golden prisms, which melt at 124°, is thus obtained. When this is boiled with a dilute solution of sodium hydrogen carbonate, it gives *nitrophenylcitraconazide*, $NO_2{\cdot}C_6H_4N_2H_2{\cdot}CO{\cdot}C_3H_4COOH$, which on subsequent treatment with sodium carbonate yields *nitrophenylhydrazine*, to be described in a future communication.

V. H. V.

Action of Phenylhydrazine on Amido-compounds of the Benzene Series. By F. Just (*Ber.*, **19**, 1207—1209).—Orthonitraniline, orthonitroparatoluidine, sulphanilic acid, and other amidoderivatives of benzene containing a nitro-group or acid radicle, react with phenylhydrazine, but not as was expected with formation of hydrazo-compounds. In the case of sulphanilic acid, for example, the acid was recovered unaltered, whilst the phenylhydrazine decomposed with formation of aniline, benzene, nitrogen, and ammonia.

N. H. M.

Phenylhydrazine and Acid Amides. By F. Just (*Ber.*, **19**, 1201—1205).—*Formylphenylhydrazine*, NHPh·NH·CHO, is obtained by heating phenylhydrazine and formamide (equal mols.) at 130° for a few minutes. It forms lustrous, colourless plates melting at 145°, sparingly soluble in cold water, benzene, and chloroform, readily in hot alcohol. When yellow mercuric oxide is added to a solution of the substance in benzene, it is at once reduced; on evaporation, the solution yields an explosive oil, probably Fischer's formyldiazobenzene.

Acetyl- and benzoyl-phenylhydrazine were prepared in a manner similar to the above compound.

Phenylhydrazine reacts readily with phthalimide at 120° with formation of Hötte's phthalylphenylhydrazine (this vol., p. 353); the author ascribes to the latter compound the constitution

$$CO<\begin{matrix}-O-\\ C_6H_4\end{matrix}>C:N_2HPh.$$

Benzenesulphonamide and Fahlberg's "saccharine" also react with phenylhydrazine. N. H. M.

Formation of Anhydro-compounds of Orthamidophenylmercaptan from Thioanilides. By P. Jacobson (*Ber.*, **19**, 1067—1077).—When Klinger's β-thiobenzaldehyde (Abstr., 1878, 132) is heated with aniline for four hours at 210—220°, thiobenzanilide, stilbene, and a small quantity of Hofmann's benzenylamidophenylmercaptan (Abstr., 1880, 386) are formed; the yield of the latter is considerably increased by heating for eight to ten hours. It is readily prepared by adding 4·26 grams of thiobenzanilide dissolved in an excess of caustic soda and diluted to about 200 c.c. to 65 c.c. of a 20 per cent. aqueous solution of potassium ferricyanide; after 24 hours the yellowish precipitate which is formed is extracted with strong hydrochloric acid; the solution when filtered and diluted with three or four times its volume of water yields a mass of white needles. The yield is about 60 per cent.

The product obtained by Leo (*Dissertation*, Bonn, 1878) by the distillation of thiobenzanilide, to which he ascribed the formula $C_{27}H_{20}N_2S_2$, was found to consist of benzenylamidophenyl mercaptan.

Thioacetanilide is conveniently prepared by rubbing together 35 grams of phosphorus pentasulphide and 54 grams of acetanilide, and then heating in a flask (of 1 litre capacity) for 15 minutes over steam. The syrupy mass is at once treated gradually with 250 c.c. of warm alcohol. When cold, it is filtered, the filtrate treated with an excess of caustic soda, four times its volume of water is added, and the whole is allowed to remain a night; the crystalline substance (about 20 per cent. of the weight of acetanilide) is separated by filtration, sulphuric acid is added to the solution until a turbidity is produced, and a current of carbonic anhydride passed through it. It is purified by dissolving it in caustic soda and precipitating with carbonic anhydride. The yield is 25—30 per cent. of the acetanilide used. When oxidised with potassium ferrocyanide, it yields ethenylamidophenyl mercaptan (Hofmann, Abstr., 1880, 885); when distilled diphenylethenylamidine is formed.

When a solution of 6·9 grams of phenylthiourethane in 50 c.c. of caustic soda (sp. gr. 1·3) is diluted to 300 c.c. and treated with 132 c.c. of a 20 per cent. solution of potassium ferricyanide, it is converted into Liebermann's phenylthiourethane sulphide (*Annalen*, **207**, 159). The latter is reconverted into phenylthiourethane when warmed with zinc-dust in acetic acid solution; this accords with the constitution ascribed to the compound by Liebermann (*loc. cit.*).

Thiocarbanilide when oxidised yields carbanilide. N. H. M.

Reaction between Oximido-compounds and Phenylhydrazine. By F. Just (*Ber.*, **19**, 1205—1207).—When methylphenylacetoxime (from acetophenone and hydroxylamine) is heated with phenylhydrazine at 150°, acetophenonephenylhydrazine is formed (compare Abstr., 1883, 798). In a similar manner, benzophenonephenylhydrazine was obtained from diphenylacetoxime and phenylhydrazine. N. H. M.

Products of the Reduction of Metanitro-α-methylcinnamaldehyde. By W. v. Miller and F. Kinkelin (*Ber.*, **19**, 1248—1252).—*Metamido-α-methylcinnamaldehyde*, $C_{10}H_{11}NO$, is obtained by adding an alcoholic solution of 5 grams of metanitro-α-methylcinnamaldehyde (this vol., p. 560) to a hot mixture of 8 grams of ferrous sulphate and ammonia. It is then filtered, and the filtrate extracted with ether; on evaporating the ether, the aldehyde remains as a yellow oil. It is obtained in crystals on adding light petroleum to the solution in ether, and allowing the mixture to evaporate in a partial vacuum. It forms yellow, moss-like aggregates of crystals, and melts at 60°; it is not stable. The *phenylhydrazine-derivative* forms slender, yellow needles, melting at 157°; the *acetyl-derivative* crystallises in short thick prisms and melts at 120°.

When metanitro-α-methylcinnamaldehyde is treated with tin and hydrochloric acid, a *base*, $NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH{<}\begin{matrix}CH\\CH\end{matrix}{>}$ is obtained. The latter crystallises from ether in colourless, lustrous plates which melt at 98°, and sublime at a slightly higher temperature; it boils at 271—272° under 718 mm. pressure. The *hydrochloride* forms colourless lustrous plates; the *platinochloride*, $(C_{10}H_{11}N)_2,H_2PtCl_6 + 2H_2O$, forms slender needles. The *acetyl-derivative* crystallises from a mixture of alcohol and ether in colourless prisms, melting at 148°. The *benzylidene-compound* is prepared by warming the base with benzaldehyde; it forms bright yellow needles, very readily soluble in alcohol and ether and melts at 73°. The base readily forms an additive compound with bromine. N. H. M.

Action of Potassium Cyanide on Nitroterephthaldehyde. By B. Homolka and W. Löw (*Ber.*, **19**, 1090—1093).—Homolka has already investigated the action of potassium cyanide on nitrobenzaldehyde (Abstr., 1884, 1342). The authors have now replaced the latter compound by Löw's nitroterephthaldehyde (Abstr., 1885, 799). In this case *azoxyterephthaldehydic acid*, $N_2O[C_6H_3(COH){\cdot}COOH]_2$, is formed, one of the aldehyde-groups (undoubtedly that in the ortho-position to the nitro-group) becoming oxidised to carboxyl, whilst the

other remains unchanged. This acid crystallises in almost colourless needles, easily soluble in alcohol, ether, and chloroform, almost insoluble in water. It begins to blacken at 240°, and decomposes completely at 280°. It has distinctly aldehydic properties, and gives a *phenylhydrazine-derivative* crystallising in orange-yellow prisms, and melting without decomposition. When oxidised by alkaline permanganate, the acid yields *azoxyterephthalic acid*, $N_2O[C_6H_3(COOH)_2]_2$, which crystallises in yellow scales, easily soluble in alcohol, ether, and boiling water, and decomposes at 250—280°. When reduced with sodium amalgam, the last-named acid yields *hydrazoterephthalic acid*, but this is so very easily oxidisable that it could not be obtained pure. An acetic acid solution of the hydrazo-acid, when gently heated with sodium nitrite, yields *azoterephthalic acid;* this is easily soluble in alcohol and ether, sparingly so in water, and decomposes above 200°. It was also prepared, for identification, from nitroterephthalic acid by the method described by Claus and May (Abstr., 1882, 515) for the preparation of azophthalic acid. When reduced with tin and hydrochloric acid, it yields amidoterephthalic acid.

L. T. T.

Action of Phosphorus Pentachloride on Hippuric Acid. By L. Rugheimer (*Ber.*, **19**, 1169—1174).—Trichloroquinoline being formed by the action of phosphorus pentachloride on malonanilidic acid (Abstr., 1884, 1050), the author considered it probable that the isomeric compound, hippuric acid, would yield derivatives of isoquinoline.

By acting on hippuric acid with phosphorus pentachloride, Schwanert (*Annalen*, **112**, 59) has obtained two compounds, C_9H_6ClNO and $C_9H_5Cl_2NO$. The author regards these as mono- and di-hydroxychlorisoquinolines; the latter of these compounds is best prepared by heating 10 parts of hippuric acid with 35 parts of phosphorus pentachloride and 20 parts of phosphorus oxychloride. The product is distilled, and the portion passing over above 130° is heated for an hour with a solution of sodium carbonate in a reflux apparatus; on cooling, crystals of the chloro-derivative separate; the yield is from 5 to 13 per cent. By heating this compound in a solution of phosphorus oxychloride with excess of phosphorus pentachloride in a sealed tube at 160—175° for three hours, a colourless, crystalline compound is obtained which, after recrystallisation from alcohol, forms foliated crystals. It melts at 133—134·5°, and has the composition $C_9H_5Cl_6N$; when heated to 100° it emits a peculiar odour, and volatilises in considerable quantity at a temperature below its melting point; the author considers it to be a dichlorisoquinoline tetrachloride. When heated with a solution of hydrogen iodide in acetic acid at 200° for six hours, isoquinoline seems to be formed.

A. P.

Isomerism on the Cinnamic Acid Series. By A. Michael and G. M. Browne (*Ber.*, **19**, 1378—1381).—By the decomposition of α-β-dibromhydrocinnamic acid, Glaser obtained two isomeric bromocinnamic acids, of which the one designated the β-acid, is readily converted into that designated the α-acid. Similar observations have been made by Plöchl (Abstr., 1883, 194) with the corresponding chloro-acids.

But as the tribromhydrocinnamic acids resulting from the combination of bromine with the above acids are not identical, but isomeric, it appears that these acids afford an example of isomerism similar to those observed in fumaric and maleic acids. It is thus probable that both acids are α-derivatives, and to obtain the true β-acid the authors have prepared a bromo-acid by the action of hydrobromic acid on phenylpropiolic acid at 0°. The acid thus obtained is isomeric with the acids previously isolated, as exemplified by the following table:—

	α-Acid.	β-Acid.	Acid from propiolic acid.
Melting point.....	130—131°	120°	158·5°.
Crystalline form ..	Long needles.....	Six-sided crystals ..	Rhombic plates.
Solubility	Very soluble in alcohol.	Very soluble in alcohol.	Sparingly soluble in alcohol and benzene.
Ammonium salt...	Needles sparingly soluble.	Deliquescent needles.	Long, non-deliquescent needles.
Barium salt.....	Rhombic leaflets...	Deliquescent needles.	Concentrically grouped prisms.
Lead salt.....	Rhombic leaflets, crystallisable from water.	Curdy precipitate, decomposed by heating with water.	Amorphous precipitate, decomposed by heating with water.

The acids also differ in their reaction with concentrated alkalis, by which the α- and β-acid are unaltered, but the new acid is converted at once into an insoluble oil. So also the tribromhydrocinnamic acid from the new acid differs from the two isomerides previously known, the properties of which are compared in the following table:—

	α-Acid.	β-Acid.	New acid.
Melting point.....	132°	151°	148°.
—	Melts with slight decomposition.	Is unaltered by fusion.	Melts with complete decomposition.
Crystalline form ..	Four-sided prisms .	Rhombic prisms...	Triclinic prisms.
Solubility, &c., in water.	Soluble in cold and hot water without change.	Soluble in cold and hot water without change.	Decomposed slowly by cold, at once by hot water to form a neutral oil.

Similarly from propiolic and hydrochloric acids, a third chlorocinnamic acid is produced, the properties of which will be described in a future communication. V. H. V.

Conversion of Ethyl Bromocinnamate into Ethyl Benzoylacetate. By A. Michael and G. M. Browne (*Ber.*, **19**, 1392—1393). Ethyl bromocinnamate dissolved in concentrated sulphuric acid, and then poured into a large excess of the acid, is converted into ethyl

benzoylacetate. It would thus appear that the acid is an α-derivative, the reactions being explained as follows:—(i) CHPh : CBr·COOEt + H_2O = OH·CHPh·CHBr·COOEt; (ii) OH·CHPh·CHBr·COOEt = OH·CPh : CH·COOEt + HBr; and (iii) OH·CPh : CH·COOEt = PhCO·CH_2·COOEt. The formation of acetophenone from α-bromostyrene can be similarly explained. V. H. V.

Substitution Products of Salicylic Acid. By E. F. Smith and E. B. Knerr (*Amer. Chem. J.*, **8**, 95—101).—*Metachloriodosalicylic acid*, OH·C_6H_2ClI·COOH.—When chlorsalicylic acid (melting at 172°) is treated with iodine in alcoholic solution, it yields chloriodobenzoic acid; but when treated with iodine and mercuric oxide, chloriodosalicylic acid is obtained. The free acid is sparingly soluble even in boiling water; it melts at 224°, and may be recrystallised from dilute alcohol in long colourless needles. The following salts are described: $C_7H_3ClIO_3Na + 2H_2O$; $(C_7H_3ClIO_3)_2Ca + 5H_2O$; $(C_7H_3ClIO_3)_2Ba + 4\frac{1}{2}H_2O$, rather difficultly soluble in water; $(C_7H_3ClIO_3)_2Mg + 5\frac{1}{2}H_2O$; $(C_7H_3ClIO_3)_2Zn + 3H_2O$; the silver salt is amorphous and insoluble. From the silver salt, the methyl and ethyl salts were prepared; both are crystalline; the first melts at 129—130°.

The authors have re-examined a dichlorosalicylic acid previously prepared by them; its melting point is again found to be 213—214°, and it is therefore different from the acid melting at 223—224° obtained by Rogers. Dichlorosalicylic acid (m. p. 213—214°), when treated with strong nitric acid in glacial acetic acid solution, yields a dichloronitrophenol having all the properties of the [1 . 2 . 4 . 6] dichlornitrophenol.

Nitrous anhydride when passed into wintergreen oil in ethereal solution, causes the separation of two crystalline substances which may be separated by cold ether. The soluble compound melts at 94°; when treated with caustic alkali, it yields α-metanitrosalicylic acid. If the insoluble compound melting at 118° is treated with caustic alkali, it yields β-metanitrosalicylic acid. H. B.

Action of Ammonium and Potassium Thiocyanates on Phthalic Acid. By O. Aschan (*Ber.*, **19**, 1398—1401).—When equal parts of phthalic acid and ammonium thiocyanate are heated at 150—160°, the whole solidifies after a few minutes; the product consisting of phthalimide. The latter is rather readily soluble in boiling glacial acetic acid, sparingly soluble in benzene. When boiled with strong hydrochloric acid, it is converted into phthalic acid. Cold concentrated aqueous ammonia converts it quantitatively into phthalyldiamide (Wislicenus, *Sitzungsber. Akad. Wiss. Munich*, 1884, 217). *Acetylphthalylimide*, $C_8H_4NO_2Ac$, is obtained by boiling the imide with an excess of acetic anhydride for 12 hours. It melts at 132—135°, and decomposes slowly at 100°; cold alkali solution and boiling water or alcohol decompose it. It is readily soluble in boiling glacial acetic acid or benzene, sparingly soluble in ether or cold alcohol.

Potassium thiocyanate also reacts with phthalic acid, yielding phthalimide. N. H. M.

Action of Phosphoric Chloride on Phthalic Anhydride. By A. Claus and R. Hoch (*Ber.*, **19**, 1187—1194).—Dichlorophthalic anhydride is obtained by heating phthalic anhydride and phosphoric chloride in molecular proportion for 12—14 hours at 170° in a sealed tube; the yield is good. A slight excess of phosphoric chloride should be employed as otherwise the product contains some unaltered phthalic anhydride, a trace of a chloro-acid being formed at the same time.

Phthalyl tetrachloride is best prepared by heating phthalic anhydride (1 mol.), with phosphorus pentachloride (2 mols.), at 245° for 14 to 15 hours (compare v. Gerichten, Abstr., 1880, 473); the product consists of a mixture of the di- and tetra-chlorophthalic anhydrides with other low boiling compounds; the fraction boiling between 268° and 271° consists of a mixture of chlorophthalic anhydrides, from which tetrachlorophthalic anhydride may be best separated by dissolving the fraction in light petroleum, and exposing this solution to the action of moist air at a low temperature; by this means, dichlorophthalic anhydride is gradually decomposed, phthalic anhydride crystallising out, and finally the tetrachloro-compound is deposited in large, colourless prismatic or tabular crystals almost pure. It is not so readily decomposed by water as is the dichloro-compound, but on exposure to the air a crust of phthalic anhydride slowly forms on the crystals. The authors have not succeeded in obtaining the isomeric compound described by v. Gerichten (*loc. cit.*), which melts at 47° and boils at 262°.

The fraction from the above reactions, boiling at 240—260°, yields pure orthochlorobenzoic acid.

If phosphoric chloride (3 mols.) be heated with phthalic anhydride (1 mol.), the same reactions take place, but dichlorobenzoic acid is also formed, and a larger quantity of phosgene gas is given off. When more phosphoric chloride is employed, and the mixture heated to 280°, carbon tetrachloride and phosgene gas are formed, together with di- and tri-chlorobenzene and mono- and di-chlorobenzoic acids; by further increasing the amount of phosphoric chloride (7 mols.), and heating at 300°, no chlorobenzoic acids, but phosgene gas, carbon tetrachloride, hexa-, penta-, tetra-, and tri-chlorobenzenes are formed.

By the action therefore of phosphoric chloride on phthalic anhydride, the side-chains are removed, the first as carbonyl chloride, and the second, at a higher temperature and with excess of phosphoric chloride, as carbon tetrachloride. A. P.

Phthalamic Acid. By O. Aschan (*Ber.*, **19**, 1401—1404).—*Phthalamic acid*, $C_8H_7NO_3$, is prepared by dissolving pure phthalamide in an excess of a 25 per cent. solution of caustic potash; after 1—2 hours, a slight excess of concentrated hydrochloric acid is added. Crystals of phthalamic acid then form on the surface of the liquid; the separation is complete in five minutes if the solution is stirred. It is then collected, washed with water, pressed between filter-paper, and dried over sulphuric acid. It forms large, clear prisms, soluble in water, readily soluble in boiling alcohol and glacial acetic acid, sparingly in ether and benzene. It melts at 148—149°, and is quite stable in dry air. When heated above its melting point, it becomes

solid (at 155°), being converted into phthalimide; this when further heated melts at 228—229°. Boiling water decomposes it quickly with formation of hydrogen ammonium phthalate; glacial acetic acid converts it into phthalic anhydride and ammonia. The *aniline salt* crystallises in needles. N. H. M.

Formation of Ethyl Succinosuccinate from Ethyl Dihydroxyterephthalate. By F. Herrmann (*Ber.*, **19**, 1174).—The author now admits that Baeyer's statement on this subject is correct (compare this vol., pp. 445 and 550).

Quinol and Formic Acid. By F. Mylius (*Ber.*, **19**, 999—1009). —*Quinolformic acid*, $C_{25}H_{26}O_{10}$, is formed when quinol (4 mols.) is dissolved in hot formic acid, and separates on cooling in colourless, pointed crystals; it melts at about 60° with evolution of formic acid. When dissolved in water, it is decomposed into its constituents.

When quinol is heated with twice its weight of crystallisable formic acid for 3—4 hours at 250°, a product is obtained consisting of glassy needles; a large quantity of carbonic oxide is formed. The new compound cannot be purified by crystallisation, as all solvents, water, alcohol, &c., decompose it into quinol and carbonic oxide, and a small quantity of formic acid. It melts at 170° with evolution of carbonic oxide, and leaves a residue of quinol. It is probably formed by the elimination of water (1 mol.) from quinolformic acid (2 mols.), and would thus be *quinolformic anhydride*, $(C_6H_6O_2)_8,C_2H_2O_3$. Concordant analytical results could not be obtained, but the results of quantitative experiments, in which the carbonic oxide and the formic acid were estimated, support this view.

Quinolhydrocyanic acid, $(C_6H_6O_2)_2,HCN$, is obtained by heating quinol with anhydrous hydrocyanic acid at 100°; it forms colourless, lustrous needles, and decomposes into its constituents when heated, or by contact with water. N. H. M.

Coumarone-α-carboxylic Acids. By A. Hantzsch and E. Lang (*Ber.*, **19**, 1298—1301).—Dimethylcoumarine was prepared by v. Pechmann and Duisberg's method (Abstr., 1884, 66) by the action of paracresol on ethyl acetoacetate. By the action of bromine, and subsequent treatment of the product with alcoholic potash this was converted into *dimethylcumarilic acid*,

$$C_6H_3Me\begin{<}\begin{matrix}CMe\\-O-\end{matrix}\end{>}C\cdot COOH.$$

The latter compound was also prepared by the action of sodium cresoxide on ethyl chloracetoacetate (compare next Abstract). It forms short prisms melting at 224—225° without decomposition, but gives off carbonic anhydride at a slightly higher temperature. The *ethyl salt* melts at 55° and boils at 298—300° under 728 mm. pressure.

Dimethylcoumarone, $C_8H_4Me_2O$ is obtained by distilling sodium dimethylcoumaronecarboxylate with lime; it boils at 210° under 728 mm. pressure.

From the results of these experiments it is concluded that acids obtained from coumarines are identical with the corresponding acids from phenols and ethyl chloracetoacetate, and further, that they are α-carboxylic acids. N. H. M.

Furfurane-derivatives of the Naphthalene Series. By A. Hantzsch (*Ber.*, **19**, 1290—1297).—Fittig and Ebert obtained (Abstr., 1883, 474) from coumarin an indifferent substance, coumarone, to which they ascribed the constitution $C_6H_4<\overset{-O-}{CH}>CH$. Rössing (Abstr., 1885, 388) obtained the same compound from aldehydophenoxacetic acid.

Ethylic β-methylcoumarilate, $C_6H_4<\overset{-O-}{CMe}>C\cdot COOEt$, is prepared by the action of ethyl chloracetoacetate (from ethyl acetoacetate and sulphuryl chloride) on sodium phenoxide; the mixture has to be kept cool after the reaction has once begun, but must ultimately be heated on a water-bath. The product is poured into water and after being diluted with ether, washed several times with water. The oil obtained by evaporating the ether, consists of ethyl phenoxylacetoacetate, COMe·CH(OPh)·COOEt; this is gradually added to an equal volume of sulphuric acid which is kept cool, and the whole after some hours poured into water; it is extracted with ether, and the solid substance obtained by evaporating off the ether and drying the residue, purified by boiling the solution in benzene with animal charcoal. It forms large, rhombic plates which melt at 51° and boils at 290° (uncorr.). *β-Methylcoumarilic acid*, $C_{10}H_8O_3$, crystallises from 50 per cent. alcohol in feathery needles or short, lustrous prisms; when carefully heated, it sublimes mostly unchanged; it melts at 188—189° with evolution of carbonic anhydride and formation of methylcoumarone. The *potassium salt* (with 1 mol. H_2O) forms thin, lustrous needles; the *ammonium salt* (with 1 mol. H_2O) crystallises in tufts of needles; the *barium* (with 3 mols. H_2O) and *silver salts* are also described.

β-Methylcoumarone, $C_6H_4<\overset{CMe}{-O-}>CH$, is obtained by distilling the above carboxylic acid. It boils at 188—189°, and is insoluble in alkalis. It does not react with hydroxylamine or phenylhydrazine. In its properties, it corresponds exactly with coumarone; on the other hand, β-methylcoumaronecarboxylic acid differs essentially from coumarilic acid, which boils without decomposition (at 310—315°) and gives up carbonic anhydride only when distilled with lime.

Sodium hydroxyphenoxide also reacts with ethyl chloracetoacetate with formation of a compound, $C_{12}H_{12}O_4$. The author intends investigating the behaviour of these furfurane-compounds towards ammonia, amines and the sulphides of phosphorus. N. H. M.

Orthohydroxyphenylsulphonic Acid. By Serrant (*Compt. rend.*, **102**, 1079—1082).—The author proposes the empirical name *sozolic acid* (*σώζω*) for this compound, instead of the name *aseptol* previously given to it, since the latter indicates an alcoholic function,

whereas orthohydroxyphenylsulphonic acid is a strong acid which forms well-defined salts. Its solubility in all proportions in water and its superiority over salicylic acid and phenol as an antiseptic, make it especially valuable. It is very rapidly eliminated from the system, and may therefore be used with great advantage where the internal administration of an antiseptic is necessary.

It is interesting to note that antiseptic properties in the benzene series seem to be confined to ortho-derivatives. Orthohydroxyphenylsulphonic acid differs from the corresponding para-derivative in the same way that salicylic acid differs from parahydroxybenzoic acid; the latter has a well-marked phenolic function and has no antiseptic properties. C. H. B.

Aromatic Sulphonamic Acids. By J. Wagner (*Ber.*, **19**, 1157—1158).—Pyridinesulphonic acid, $C_5H_4N\cdot HSO_3$, may be prepared by acting on pyridine with ethyl chlorosulphonate, chlorosulphonic acid, or sulphuryl chloride; it is decomposed by water or alkalis, pyridine sulphate and sulphuric acid being formed; it is readily soluble in aniline, with which it reacts, forming aniline sulphanilate,

$$NH_2\cdot C_6H_4\cdot HSO_3,NH_2Ph;$$

this may be extracted by means of ether; it melts at 192° and is readily decomposed by water, aniline sulphate being formed. On boiling the solution of this salt in aniline, aniline sulphate and a compound, $C_{18}H_{19}N_3S_2O_5$, which is probably phenylamidosulphurylphenylsulphonamate, are formed. On adding sodium ethide to an alcoholic solution of aniline phenylsulphonamate, a crystalline precipitate of sodium sulphanilate is formed. A. P.

Nitration Products of Metaxylenesulphonic Acid [1 : 3 : 4]. By A. Claus and E. Schmidt (*Ber.*, **19**, 1418—1427).—It has been shown by Harmsen (Abstr., 1881, 49) and also by Limpricht (Abstr., 1885, 1234) that metaxylenesulphonic acid [$SO_3H = 4$], when nitrated, yields the same nitro-acid as is obtained by the sulphonation of nitroxylene [$Me_2 : NO_2 = 1 : 3 : 4$]. This acid therefore has the constitution [$Me_2 : SO_3H : NO_2 = 1 : 3 : 4 : 6$]. The authors find that the two other possible isomeric nitro-acids in which the nitro-groups occupy the 2 and 5 position respectively, are also formed in the reaction, the latter, however, only in small quantity. A method for the separation of the three acids is described. The copper and silver salts of the [$NO_2 = 6$] acid are described; it is also found that the sulphonamide melts at 187°, not at 179° as stated by Limpricht (*loc. cit.*).

The *nitroxylenesulphonic acid*, [$Me_2 : SO_3H : NO_2 = 1 : 3 : 4 : 2$] crystallises with 1 mol. H_2O in small plates, becomes anhydrous at 100°, melts at 144°, and is readily soluble in water, alcohol, and nitric acid, insoluble in pure ether and chloroform, sparingly soluble in sulphuric acid, from which it crystallises in anhydrous plates. The barium salt, $(C_8H_8NO_2\cdot SO_3)_2Ba$, crystallises in large anhydrous plates, sparingly soluble in boiling water. The potassium, sodium, calcium, lead, copper and silver salts are described. The *chloride*,

$C_8H_8NO_2{\cdot}SO_2Cl$, crystallises in large, colourless prisms, melts at 96° (uncorr.), and is very soluble in ether. The *sulphonamide*, $C_8H_8NO_2{\cdot}SO_2NH_2$, forms colourless needles or prisms, melts at 172° (uncorr.), and is readily soluble in ether and alcohol.

The *nitroxylenesulphonic acid* [$Me_2 : SO_3H : NO_2 = 1 : 3 : 4 : 5$] crystallises in small nodules formed of colourless plates, and melts at 95—100°. Its salts are very soluble in water, and do not crystallise so well as those of its isomerides: the much greater solubility of its barium salt is utilised in the separation of the mixed acids. The potassium, sodium, barium, calcium, lead, copper, and silver salts are described. The *chloride*, $C_8H_8NO_2{\cdot}SO_2Cl$, forms colourless plates, melts at 97° (uncorr.), is readily soluble in ether, alcohol, chloroform, benzene, &c., and is more quickly decomposed by water than its isomerides. The *amide*, $C_8H_8NO_2{\cdot}SO_2NH_2$, crystallises in small, colourless needles, melts at 108° (uncorr.), and is readily soluble in alcohol, ether, &c.

A dinitro-xylenesulphonic acid was obtained by Limpricht and Gronow (Abstr., 1885, 1234) by the nitration of metaxylenesulphonic acid; the authors have also formed it by the nitration of the 2 and the 6 mononitro-acids; it must therefore have the constitution [$Me_2 : (NO_2)_2 : SO_3H = 1 : 3 : 2 : 6 : 4$].

An isomeric *dinitro-acid* [$(NO_2)_2 = 5 : 6$] is obtained, together with that above mentioned, by treating a solution of metaxylenesulphonic acid in acetic acid with a mixture of 3 parts of fuming nitric, 3 parts of fuming sulphuric acid, and 1 part of phosphoric anhydride. It forms an indistinctly crystalline mass, melts at 60—70°, and is very soluble in water. The potassium, sodium, barium, calcium, lead, and copper salts are described. The *chloride*, $C_8H_7N_2O_4{\cdot}SO_2Cl$, forms an indistinctly crystalline mass and melts at 117—118° (uncorr.). The *amide*, $C_8H_7N_2O_4{\cdot}SO_2NH_2$, crystallises in small, colourless needles, and melts at 158° (uncorr.). A. J. G.

Pseudocumenesulphonic Acids and Bromopseudocumenesulphonic Acids. By O. Jacobsen (*Ber.*, **19**, 1218—1223).—*Monobromopseudocumenesulphonic acid*, $C_6HMe_3Br{\cdot}SO_3H$ [$=1 : 3 : 4 : 6 : 5$], is obtained by dissolving bromopseudocumene (m. p. 73°) in warm slightly fuming sulphuric acid. The *sodium salt* (with 1 mol. H_2O) forms flat needles with a glassy lustre, rather sparingly soluble in cold water. The *calcium salt* (with 3 mols. H_2O) crystallises in slender needles. The *amide* forms voluminous slender needles which melt at 186°; it is readily soluble in alcohol.

Pseudocumenesulphonic acid, $C_6H_2Me_3{\cdot}SO_3H$ [$= 1 : 3 : 4 : 5$], is prepared by treating powdered sodium monobromopseudocumenesulphonate with aqueous ammonia and zinc-dust. The *barium* and *sodium* (with $1\frac{1}{2}$ mols. H_2O ?) salts were prepared. The *amide* has all the properties of that obtained from durene, melting at 170—172° (compare this vol., p. 694). When the sodium salt is fused with potash, pseudocumenol melting at 95° is formed (compare Abstr., 1885, 772); the dibromo-derivative melts at 152°. On prolonged fusion with potash, pseudocumenol yields *hydroxy-xylylic acid*,

$$OH{\cdot}C_6H_2Me_2{\cdot}COOH\ [Me_2 : COOH : OH = 1 : 3 : 4 : 5].$$

This forms slender needles with a silky lustre melting at 187°; the solution of the acid, when treated with ferric chloride, acquires a violet-blue colour.

Dibromopseudocumene [$Me_3 : Br_2 = 1 : 3 : 4 : 5 : 6$] is obtained by treating crystalline monobromopseudocumene in the cold by gaslight with the theoretical amount of bromine; after some hours, the solid mass is washed with water, treated with caustic soda, again washed, and dried on a porous plate. The product is distilled, and the fraction boiling at 292—300° is fractionally crystallised from light petroleum; the tribromo-derivative formed in the reaction separates first, and then dibromopseudocumene. The latter was purified by recrystallisation from alcohol. It melts at 63—64°, and has the properties ascribed to it by Schramm (this vol., p. 451). The *sulphonic acid* [$Me_3 : Br_2 : SO_3H = 1 : 3 : 4 : 5 : 6 : 2$] was prepared by adding an excess of chlorosulphonic acid to the dibromide heated at its melting point. After 1 to 2 hours, ice and water are added and the insoluble product washed successively with water and with alcoholic soda. The *sodium salt* so obtained crystallises from water, in which it is very sparingly soluble, in small lustrous scales. The *barium salt* and the *amide* melting above 250° with decomposition are described. When the sodium salt is reduced with zinc and ammonia, *sodium pseudocumenesulphonate* [$Me_3 : SO_3Na = 1 : 3 : 4 : 2$] is obtained; it forms very small plates, and is very soluble. The amide is identical with the second amide obtained from durene (*loc. cit.*). It melts at 113°, but not sharply. When heated with hydrochloric acid at 170°, it yields pseudocumene. *Pseudocumenol* [$Me_3 : OH = 1 : 3 : 4 : 2$] forms long needles, melting at 62° and boiling at 232—234°; it gives no coloration with ferric chloride. *Sodium bromopseudocumenesulphonate* [$Me_3 : Br : SO_3Na = 1 : 3 : 4 : 5 : 2$], which is formed in the preparation of the dibromosulphonic acid from dibromopseudocumene, crystallises with $\frac{1}{2}$ mol. H_2O in large, lustrous plates, very readily soluble in hot water. The *amide* crystallises from dilute alcohol in long slender needles, melting at 158°. When the sodium salt is reduced, sodium pseudocumenesulphonate [$SO_3H = 2$] is formed. Hydrochloric acid at 170° saponifies the amide, with formation of *monobromopseudocumene* [$Me_3 : Br = 1 : 3 : 4 : 5$], boiling at 236—238°; it could not be solidified. N. H. M.

Oxidation of Aromatic Sulphinic Ethers to Sulphonates. By R. Otto and A. Rössing (*Ber.*, **19**, 1224—1227; compare Abstr., 1885, 1232).—7·8 grams of ethyl benzenesulphinate (containing a little ethyl phenylsulphoformate) were dissolved in 20 times the volume of glacial acetic acid, and a hot saturated solution of 4·8 grams of potassium permanganate in 25 per cent. acetic acid gradually added, the whole being continually shaken. It was then decolorised with alcohol, diluted with water, and extracted repeatedly with ether. The extract was treated with sodium carbonate solution to remove acetic acid; on evaporating the ether, a yellowish oil was obtained having the properties of ethyl benzenesulphonate (this Journal, 1877, i, 463). By boiling with aqueous caustic potash, this was decomposed into alcohol and potassium benzenesulphonate.

In a similar manner, ethyl paratoluenesulphinate was oxidised to the sulphonate.

The mode of formation of the alkyl sulphinates makes it probable that they are derivatives of acids of the formula R·SO·OH rather than R·SO_2·H. N. H. M.

Products of the Hydrolysis of Ethereal Thiosulphonates. By R. Otto and A. Rössing (*Ber.*, **19**, 1235—1242).—When phenylthiobenzenesulphonate is saponified with potash or baryta, it yields phenyl disulphide, a salt of benzenesulphinic acid, and a trace of thiophenol; no benzenesulphonic acid is formed. Tolyl and ethyl parathiotolylsulphonates and ethyl thiobenzenesulphonate behave similarly when saponified. N. H. M.

α-Phenylindole. By A. Pictet (*Ber.*, **19**, 1063—1066).—By passing benzylideneorthotoluidine through a red-hot tube, Étard obtained (Abstr., 1883, 179) a compound to which he ascribed the constitution $C_6H_3Me<^{-C_6H_4-}_{N:CH}>$. The author prepared the same compound by adding phenyl benzyl ketone to fuming nitric acid (4 parts) kept cool with ice; the product was poured into water, and the oil thus obtained, consisting chiefly of orthonitrophenyl benzyl ketone, was treated with ammonia and zinc-dust. When the reaction was completed, the whole was agitated with ether, the ethereal solution extracted with dilute hydrochloric acid and evaporated. The formation of the substance from the unstable orthamido-phenyl benzyl ketone, $NH_2·C_6H_4·CH_2·COPh$, together with the analogy with methylketole (Baeyer and Jackson, Abstr., 1881, 734), point to the constitution $C_6H_4<^{CH}_{NH}>CPh$ as the most probable. It is therefore phenylindole. Its preparation from benzylideneorthotoluidine is very simple, and the yield is 30 per cent. of the benzylidinetoluidine employed. It crystallises from carbon bisulphide in colourless plates which melt at 187°; it boils above 360° and sublimes readily. It dissolves very readily in ether, chloroform, and benzene, &c.; sparingly in hot water. The alcoholic solution gives an intense violet coloration to pine-wood moistened with hydrochloric acid. The solution in sulphuric acid is colourless, but becomes red on addition of a drop of nitric acid. α-Phenylindole is a very weak base; it dissolves only in concentrated hydrochloric acid, and is precipitated by water. The *platinochloride* forms small, red needles. When reduced, it yields a liquid *dihydro-compound*. Potassium permanganate and chromic mixture have scarcely any action on it. N. H. M.

Carrotene. By A. Arnaud (*Compt. rend.*, **102**, 1119—1122).—The author has previously shown that carrotene is identical with the orange-red crystalline substance which can be obtained from leaves, and which also exists in many fruits, especially the tomato.

In order to prepare carrotene, carrots are rasped and pressed, and the juice mixed with lead acetate, which precipitates the carrotene in the form of a lake. The precipitate is dried in a vacuum and extracted

with carbon bisulphide, which is then evaporated, and the residue treated systematically with cold light petroleum. The pressed pulp is also treated with the same solvents, and the crude carrotene is dissolved in carbon bisulphide, precipitated by adding alcohol, and recrystallised from benzene.

Carrotene has the composition $C_{26}H_{38}$(C 88·67, H 10·63 per cent.), and crystallises in rhombic plates with a metallic lustre, blue by reflected light and orange-red by transmitted light. It decomposes above 300° in a vacuum, and forms a colourless, viscous liquid. It combines readily with oxygen, chlorine, and bromine. If carrotene is dissolved in dry benzene and mixed with iodine, the di-iodide $C_{26}H_{38}I_2$ is obtained in deep green crystals with a coppery lustre. Carrotene oxidises in the air even at the ordinary temperature, oxidation taking place very rapidly if the carrotene is in solution or if it is heated to 70°. The product is soluble in cold alcohol, but only slightly soluble in carbon bisulphide, and does not crystallise from its alcoholic solution. It melts at 125°, and has the composition C 70·10, H 8·57, O 21·42.

It follows from these results that carrotene is not an oxygen compound but an unsaturated hydrocarbon, and the author proposes to change the name carrotine previously assigned to it. It dissolves in concentrated sulphuric acid with formation of an intense indigo-blue solution.

The carrotene analysed by Husemann must have undergone considerable oxidation. Husemann's hydrocarrotene is really vegetable cholesterin, $C_{26}H_{44}O,H_2O$. C. H. B.

Composition of Magdala-red. By P. Julius (*Ber.*, **19**, 1365—1367).—Hofmann (*Ber.*, **2**, 374 and 412) classified Magdala-red with the rosaniline-group, assigning to it the composition $C_{30}H_{21}N_3HCl,H_2O$; the persistent retention of a molecule of water above 100 presents a further point of resemblance between the dye and the rosanilines. But since these experiments were made, two new classes of dyes have been discovered, namely, the indulines and safranines, formed in the same reaction, and consisting of the same components. The analogies of the latter with Magdala-red, as regards their chemcial properties, the stability of their salts, and the strong fluorescence of their alcoholic solutions, have been remarked upon by Nietzki. In order to determine how far the analogy is supported by the composition of Magdala-red, the author has prepared with care a specimen of its hydrochloride; a careful nitrogen determination made with the salt showed that it contained four and not three atoms of nitrogen; its composition is thus $C_{30}H_{21}N_4Cl$, a result confirmed by an analysis of the platinochloride. Hoffmann in his paper remarks on the difficulty experienced in completely burning the hydrochloride. Thus, Magdala-red belongs to the safranine class, and its formation from amido-azonaphthalene and naphthylamine hydrochloride is perfectly analogous to that of safranine from amidoazotoluene and toluidine hydrochloride (Nietzki, this Journal, 1877, ii, 454; Witt, *ibid.*, 453).

V. H. V.

Thionaphthen. By V. Meyer (*Ber.*, **19**, 1432).—With reference to Hantzsch's remark (*Ber.*, **19**, 1290) that the thiophen of the naphthalene series is still unknown, the author states that A. Biedermann has obtained the compound $OH\cdot C_6H_4<\begin{matrix}-S-\\ CH\end{matrix}>CH$ by the condensation of thiophenaldehyde with succinic acid. The author also is endeavouring to prepare thionaphthen by the action of phosphorus sulphide on coumarone. A. J. G.

Purification of Naphthalene by Means of Soap Solution. By G. Link (*Dingl. polyt. J.*, **260**, 95).—Crude naphthalene is subjected to hydraulic pressure in the cold, distilled, and the product agitated for some time with a solution of soap at 85°. The purified mass is drawn off, cooled to 50° by the addition of cold water, filtered, washed, and distilled. D. B.

β-Heptachloronaphthalene and β-Pentachloronaphthalene. By A. Claus and C. Wenzlik (*Ber.*, **19**, 1165—1169).—The β-heptachloronaphthalene described by Claus and Lippe (Abstr., 1883, 921) is best prepared by heating 1 part of tetrachloronaphthaquinone with 2 parts of phosphorus pentachloride at 250° for 6 to 8 hours in a sealed tube; the product after washing with water and alkali is purified by repeated crystallisation from alcohol, and is finally sublimed: thus obtained, it forms small, colourless needles, and melts at 194° (uncorr.); it is neither so soluble in the usual solvents nor so readily distilled with steam as are the lower chloronaphthalenes.

By heating 1 part of β-heptachloronaphthalene with 12 parts of concentrated nitric acid (sp. gr. = 1·5) in a sealed tube at 100° for 5 to 6 hours, a mixture of unaltered heptachloronaphthalene, tetrachlorophthalic acid, and β-pentachloronaphthaquinone,

$$C_8HCl_5O_2\ [Cl_5 : O_2 = 2 : 1' : 2' : 3' : 4' : 4 : 1],$$

is formed. The tetrachlorophthalic acid is removed by treating the mixture with very dilute alcohol, and the unaltered heptachloronaphthalene then dissolved out by means of boiling alcohol (90 per cent.) The pentachloronaphthaquinone is purified by recrystallisation from chloroform; it is obtained in golden-yellow lustrous scales, sublimes in long, lustrous needles, and melts at 217° (uncorr.); by further oxidation, it is converted into tetrachlorophthalic acid; by dissolving it in alcoholic potash or soda, the respective metallic derivative of tetrachlorohydroxynaphthaquinone, $OH\cdot C_8HCl_4\cdot O_2$ [$Cl_4 : O_2 : HO = 1' : 2' : 3' : 4' : 1 : 4 : 2$], is formed. To obtain the pure compound, the alcoholic solution of the alkaline salt is evaporated to dryness, then redissolved in water, and the resinous bye-products present precipitated by the addition of a solution of alum, the tetrachlorohydroxynaphthaquinone is precipitated from the clear solution by the addition of concentrated hydrochloric acid, washed with cold water and sublimed. It forms yellow needles, melts at 265° (uncorr.), is slightly soluble in cold water forming a red solution, but is insoluble in saline solutions; its alkaline derivatives are readily soluble in water, and on the addition of salts of silver,

copper, lead, &c., yield voluminous red precipitates, which form brown powders when dry.

Tetrachloronaphthaquinone-anilide crystallises from alcohol or glacial acetic acid in magnificent, lustrous, dark red scales, and melts at 240° (uncorr.).

By heating pentachloronaphthaquinone with phosphorus pentachloride in a sealed tube at 250° for six hours, perchloronaphthalene is formed. A. P.

Chlorinated α-Naphthaquinones. By A. Claus (*Ber.*, **19**, 1141—1144).—When tetrachloronaphthaquinone (Abstr., 1883, 921) is boiled with alcoholic potash, *trichlorhydroxynaphthaquinone*, $C_{10}H_3Cl_3O_3$, is formed. This substance crystallises in yellow needles, easily soluble in alcohol and ether, sparingly so in water, and melts at 235° (uncorr.). It sublimes without change, but gradually becomes coloured by exposure to the air. Its salts are intensely coloured, varying from pure red to brownish-red. The *anilide* forms lustrous copper-coloured needles, insoluble in water, and gives a violet coloration when boiled with alkalis. The *orthotoluide* melts at 205°, the *paratoluide* at 303° (uncorr.).

When dichlor-α-naphthaquinone is heated with manganese dioxide and hydrochloric acid in closed tubes at 230°, it forms an additive product, $C_{10}H_4Cl_4O_2$. This compound crystallises in large colourless prisms, melting at 117°. It is very stable towards alkalis, only being decomposed by continued boiling with concentrated potash. Nascent hydrogen easily re-forms the dichloroquinone. When treated with stannous chloride, the dichloroquinone is first formed, but if more stannous chloride is added a *dichlor-α-naphthaquinol*, $C_{10}H_4Cl_2(OH)_2$, is produced. From these properties, which differ from those of the halogen-additive derivatives of naphthalene, the author is inclined to look upon this tetrachloro-compound as a quinol, in which the two hydroxylic hydrogens are replaced by chlorine, and proposes for it the name *dichlor-α-naphthachloroquinol*, $C_{10}H_4Cl_2(OCl)_2$. Similar compounds have been obtained with tetra- and penta-chloronaphthaquinone, and are now being investigated. Dichlor-α-naphthaquinol is easily soluble in alcohol, ether, chloroform, and glacial acetic acid, crystallises in colourless needles, and melts at 135°. When exposed to the air it turns violet-brown, and if then crystallised from ether yields violet-brown needles of a quinhydrone, $C_{20}H_{10}Cl_4O_4$. Both this and the quinol are reconverted into the quinone by oxidising agents. The action of stannous chloride gives a ready method for the preparation of naphthaquinols. L. T. T.

Azo-compounds of Naphthalene. By R. Nietzki and O. Goll (*Ber.*, **19**, 1281—1284).—*β-Amidoazonaphthalene* is easily prepared from β-naphthylamine, in a manner similar to that of the α-compound from α-naphthylamine; it forms red needles, melting at 156°; the solution in sulphuric acid has a violet colour. When a solution of 15 grams of β-amidoazonaphthalene in 90 grams of sulphuric acid and 90 grams of water is treated with a concentrated solution of

5 grams of sodium nitrite, being kept cool with ice, hydroxyazonaphthalene is obtained identical with that formed by the action of β-diazonaphthalene on β-naphthol. This is regarded as a proof that β-amidoazonaphthalene does contain an amido-group. N. H. M.

Naphthoic Acids. By A. G. Ekstrand (*Ber.*, **19**, 1131—1139).—In a former paper, the author described a compound obtained by the reduction of mononitro-α-naphthoic acid, to which he ascribed the formula $C_{10}H_6<^{CO\cdot NH}_{NH\cdot CO}>C_{10}H_6$. He now thinks that the simpler formula $C_{10}H_6<^{CO}_{NH}>$ is more probable, and proposes for this substance (from its analogy with carbostyril) the name *naphthostyril*.

When mononitro-α-naphthoic acid is dissolved in a well cooled mixture of sulphuric and fuming nitric acids, it yields β-trinitronaphthalene, together with a small quantity of *trinitro-α-naphthoic acid*, $C_{10}H_4(NO_3)_3\cdot COOH$, which crystallises in brown needles melting at 283°, and has an intensely bitter taste. When heated with fuming hydrochloric acid in sealed tubes at 140—150°, the mononitro-acid suffers reduction and yields *dichloronaphthostyril*, $C_{10}H_4Cl_2<^{NH}_{CO}>$. This compound was also formed by the direct action of chlorine on naphthostyril It crystallises in yellow needles, soluble in boiling alcohol, and melts at 264—265°. Chlorinated naphthostyrils are also formed in small quantities during the reduction of the mononitro-acid, in alcoholic solution, by tin and hydrochloric acid.

Monobromo-α-naphthoic acid is obtained by treating a hot acetic solution of α-naphthoic acid with bromine. It crystallises in white needles, melting at 246°. When treated with fuming nitric acid, it yields *bromonitronaphthoic acid*, $C_{10}H_5Br(NO_2)\cdot COOH$, which crystallises in small, yellow prisms, melting at 260°. When this acid is reduced with ammoniacal ferrous sulphate, it yields monobromonaphthostyril, $C_{10}H_5Br<^{NH}_{CO}>$, crystallising in brown needles and melting at 257°. *Dibromonaphthostyril* was obtained by acting on naphthostyril suspended in water with excess of bromine. It crystallises from boiling alcohol in yellow needles, melting at 268—270°. *Acetonaphthostyril*, $C_{10}H_6<^{NAc}_{CO}>$, formed by heating amido-α-naphthoic acid with excess of acetic anhydride, crystallises from boiling alcohol in thin, white needles melting at 125°. *Dibromacetonaphthostyril*, obtained from the action of acetic anhydride on dibromonaphthostyril, forms small, yellow needles melting at 185°.

By means of the diazo-reaction, amido-α-naphthoic acid was converted into *hydroxy-α-naphthoic acid*, $OH\cdot C_{10}H_6\cdot COOH$. The best yield was obtained by dissolving the amido-acid in dilute potash, adding the calculated quantity of potassium nitrite and slowly pouring the mixture into sulphuric acid cooled with ice. The free acid melts at 169° and forms small needles, which are very soluble in alcohol and ether, easily so in water. No lactone was formed by

boiling an alcoholic solution of the acid, but when melted the acid yielded *naphtholactone*, crystallising in long, colourless needles and melting at 108°. This is rather less soluble in alcohol and ether than the hydroxy-acid and sublimes unchanged. When dissolved in carbon bisulphide and treated with bromine, it yields *monobromonaphtholactone*, which forms small, white needles melting at 192°.

L. T. T.

α-Naphtholdi- and tri-sulphonic Acids. By A. Claus and P. Mielcke (*Ber.*, **19**, 1182—1187).—The mixed α-naphtholdi- and tri-sulphonic acids obtained by Schultze (*Inaug. Dissert.*, Freiburg, 1883) by adding α-naphthol in small portions to five times its weight of fuming sulphuric acid, may be most conveniently separated from one another by converting them into the chlorides and treating with ether, in which the α-naphtholdisulphonic chloride dissolves, whilst the triosulphonic chloride is almost insoluble. To determine the position of the SO_3H-group in the naphthol radicle, the authors converted the sulphonic chloride into the corresponding trichloronaphthalene, by heating with phosphorus pentachloride (3 mols.) for several hours in a closed vessel at 170—180°; if heated above this temperature, only resinous compounds are formed, whilst the reaction does not take place at all below 170°. The product is identical with the trichloronaphthalene obtained by Faust and Saame (this Journal, 1872, 64); the α-naphtholdisulphonic acid therefore probably has the constitution $[HO : (SO_3H)_2 = 1 : 2 : 4]$.

A tetrachloronaphthalene may be prepared by heating α-naphthotrisulphonic chloride with 4 mols. of phosphorus pentachloride in a sealed tube for one and a half hours at 210—220°, and afterwards raising the temperature to 250° for an hour, then cooling to 200° and heating for an hour longer, the product is distilled with steam, boiled with soda, and further purified by repeated crystallisation from alcohol and fractional sublimation. It crystallises in colourless feathery needles, melts at 140° (uncorr.), is insoluble in water and cold alcohol, but dissolves in most other solvents. When heated with nitric acid (sp. gr. = 1·5) in a sealed tube at 110°, α-dichloro-α-naphthaquinone is formed; the constitution of α-naphtholtrisulphonic acid is therefore $[OH : (SO_3H)_3 = 1 : 2 : 3 : 4]$. Phthalic acid and chlorophthalic acid are formed by the oxidation of tetrachloronaphthol.

When α-naphtholtrisulphonic chloride is heated at 250° with 7—8 mols. of phosphorus pentachloride, octachloronaphthalene is formed, sulphur being precipitated and sulphurous anhydride given off.

A. P.

Furfurane-compounds of the Phenanthrene Series. By A. Hantzsch and G. Pfeiffer (*Ber.*, **19**, 1301—1305).—The sodium compounds of α- and β-naphthol react with ethyl chloracetoacetate just as sodium phenoxide does (compare p. 707). The crude ethylic naphthoxylacetoacetates, when added to sulphuric acid, solidify to a crystalline mass of the ethyl furfuranecarboxylate. The product is stirred with water, extracted with ether, and the residue obtained by evaporating the ether crystallised from alcohol.

Ethylic methyl-α-naphthofurfuranecarboxylate,

$$C_{10}H_6<\begin{matrix}CMe\\ -O-\end{matrix}>C\cdot COOEt\ [Me : COOEt = 2 : 1],$$

forms lustrous, flat needles melting at 108°; it dissolves readily in ether and in hot alcohol. The *free acid* forms white, microscopic plates, sparingly soluble in water and other indifferent solvents. It melts at 243—245° with evolution of carbonic anhydride. The salts, with the exception of the alkali salts, are sparingly soluble. When the ethyl salt is evaporated to dryness with an excess of alcoholic potash and then distilled, *methyl-α-naphthofurfurane*, $C_{12}H_7MeO$, is formed. This melts at 34—35° and boils at 297—299° (uncorr.); it dissolves readily in the usual solvents, and separates as an oil, which only solidifies when brought into contact with a crystal of the substance. It sublimes slowly at the ordinary temperature, has an aromatic odour, and resinifies gradually when exposed to the air. The solution of the substance in sulphuric acid is yellowish-green; when warmed this changes to green, and finally, with evolution of carbonic anhydride, to an intense purple-violet. When diluted with water, the colour of the solution changes to green.

Ethylic methyl-β-naphtho-α-furfuranecarboxylate,

$$C_{10}H_6<\begin{matrix}-O-\\ CMe\end{matrix}>C\cdot COOEt,$$

resembles its isomeride above described; it melts at 100°. The *free acid* also resembles the acid from α-naphthol; it melts at 253—254°. The *sodium salt* crystallises with 4 mols. H_2O from its solution in hot dilute caustic soda in lustrous needles with a bluish fluorescence. *Methyl-β-naphtho-α-furfurane*, $C_{12}H_7MeO$, melts at 59°, and becomes brown when exposed to air. Towards sulphuric acid, it behaves like the α-derivative, except that the colour produced on heating is a pure blue. N. H. M.

Chloro- and Bromo-derivatives of Anthracene. By W. Hammerschlag (*Ber.*, **19**, 1106—1110). — *Dichlorodibromanthracene tetrabromide*, $C_{14}H_6Cl_2Br_6$, prepared by exposing dichlorodibromanthracene to bromine-vapour, crystallises in white, lustrous needles melting at 212°, and soluble in boiling acetic acid. *Tetrabromodichloranthracene*, $C_{14}H_4Cl_2Br_4$, forms golden-yellow needles melting at 380°, and very sparingly soluble in the usual solvents. It does not absorb bromine, dissolves with violet coloration in fuming sulphuric acid, and is oxidised by chromic mixture to tetrabromoquinone. The author has noticed that although halogen-substituted anthracenes are only oxidised to quinones, their tetrachlorides and tetrabromides are readily oxidisable to substituted phthalic acids (?), and suggests this reaction as probably offering a means of determining the constitution of substituted anthracenes.

Several corrections are given:—Dichloranthracene tetrabromide melts at 178° (Schwarzer gives 166°); dibromanthraquinone melts at 265° (Diehl gives 236·5°); dichloranthracene tetrachloride melts, with evolution of hydrogen chloride, at 187° (Diehl gives 143—145°,

Liebermann and Lindemann 205—207°); tetrachloranthracene melts at 164° (Liebermann and Graebe's preparation melting at 220° probably contained higher chlorinated derivatives); dichloroanthraquinone crystallises from boiling glacial acetic acid in golden-yellow needles melting at 205°. L. T. T.

Pyrene. By E. Bamberger and M. Philip (*Ber.*, **19**, 1427—1431).—In pyrenequinone, the carbonyl-groups seem not to be directly united to one another, inasmuch as it does not show the reactions of an ortho-diketone.

Pyrenic acid, $C_{12}H_6(CO)(COOH)_2$ [$(COOH)_2 = 1:2$]. Hintz has stated that on oxidation with chromic acid pyrene yields in addition to pyrenequinone another substance of the formula $C_{15}H_8O_4$. The authors find that this substance is the anhydride of pyrenic acid, and is not formed directly, but from the free acid during the crystallisation from acetic acid to which Hintz subjected it during its purification. Pyrenic acid crystallises in golden-yellow plates, which are converted into the anhydride by heating at 120° or by crystallisation from acetic acid. The acid yields crystalline precipitates with hydroxylamine and phenylhydrazine.

The *imide*, $C_{13}H_6O<\begin{matrix}CO\\CO\end{matrix}>NH$, is formed by dissolving the acid in ammonia, and quickly separates in shimmering brass-yellow plates. A. J. G.

Choleic Acid. By P. Latschinoff (*Ber.*, **19**, 1140).—This acid is soluble at 20° in 22,000 parts of water, 750 parts of ether, 14·1 parts of 98·5 per cent. alcohol, and 25 parts of 75 per cent. alcohol. Its barium salt dissolves at the same temperature in 1200 parts of water, the solubility rapidly increasing with rise of temperature. It is dextrorotatory, giving $[\alpha]_D = +56°\,40'$. The determination was made at 20°, with a 300 mm. column of a 6·06 per cent. alcoholic solution of sp. gr. 0·811; the rotation observed being + 8° 10′. L. T. T.

Nitro-compounds of the Pyrroline Series. By G. Ciamician and P. Silber (*Ber.*, **19**, 1078—1081; comp. Abstr., 1885, 992).—*Mononitropyrrylene dimethyl diketone*, $C_8H_8N_2O_4$, is prepared by adding finely powdered pyrrylene dimethyl ketone in small quantities (3 grams) to an excess of fuming nitric acid (1·50 cm.) kept cool by cold water. The product is poured into water and extracted with ether; the ethereal solution yields an oil which soon becomes almost solid. This is recrystallised and further purified by sublimation. It forms long, white needles, melting at 149°; it is readily soluble in ether, alcohol, and hot water, and dissolves in alkaline carbonates.

When finely powdered carbopyrrolic acid is added to a large excess of fuming nitric acid kept a temperature of − 18°, dinitropyrroline (*loc. cit.*), melting at 152°, is formed. The latter, when pure, is almost colourless; the yield is 6 grams from 10 grams of carbopyrrolic acid. The mother-liquor obtained in purifying this compound was found to contain a small quantity of a second *dinitropyrroline*. The latter crystallises from water in long needles, which melt with decomposition

at 173°; it is soluble in ether, alcohol, and hot benzene. The yield is only 0·6 gram from 14 grams of carbopyrrolic acid. N. H. M.

Action of Acetic Anhydride on Homopyrroline (Methylpyrroline). By G. Ciamician and P. Silber (*Ber.*, **19**, 1408—1412; comp. *Ber.*, **14**, 1056).—Homopyrroline was obtained from the fraction of coal oil boiling above 140°, and isolated by the method previously mentioned (this vol., p. 367). If excess of potash is not used and the operation is repeated several times, the higher pyrrolines collect in the products of the last operations. The mixture of the higher pyrrolines is steam-distilled and then fractioned; the portion boiling at 140—153° contains the homopyrroline.

Methylpyrryl methyl ketone (*pseudacetylhomopyrroline*),

$$(NH)C_4H_2Me\cdot COMe,$$

is obtained by boiling 25 grams of homopyrroline (boiling at 140—153°) with 150 grams of acetic anhydride and 30 grams of freshly fused sodium acetate for 6—8 hours. The product is distilled in a partial vacuum in a water-bath to remove the excess of acetic anhydride, and steam-distilled. The residue is neutralised with sodium carbonate and extracted with ether; the oil obtained by evaporating the ether yields the solid substance when distilled. It crystallises from hot water in small white needles, melts at 85—86°, and boils at 240°. It dissolves readily in ether, alcohol, and benzene, &c. Hot caustic potash solution does not decompose it. The *silver compound*, $(NAg)C_4H_2Me\cdot COMe$, forms a white precipitate.

Acetylhomopyrroline, C_7H_9NO, is obtained as a yellow oil on distilling the crude product of the above reaction with steam. By fractional distillation of the oil, two fractions were obtained, boiling at 196—197° and at 202—203° respectively; both yielded results on analysis which point to the formula C_7H_9NO. They are almost insoluble in water and are readily saponified by caustic alkalis.

The substance described by Weidel and Ciamician (Abstr., 1880, 403) as a "homoacetyl-compound," is a mixture of the two isomerides.

When pyrryline dimethyl diketone is oxidised with potassium permanganate, a *carbopyrrylglyoxylic acid*, $COOH\cdot C_4H_2(NH)\cdot CO\cdot COOH$, is formed; the methyl salt melts at 144—145°. When fused with potash this yields a *pyrrolinedicarboxylic acid*,

$$COOH\cdot C_4H_2(NH)\cdot COOH;$$

the methyl salt melts at 132°. The authors hope to be able to show by the oxidation of methylpyrryl methyl ketone, whether the methyl and acetyl groups contained in it have the same position as the two acetyl-groups in pyrrylene dimethyl ketone. N. H. M.

Synthesis of Isocinchomeronic Acid. By L. Weiss (*Ber.*, **19**, 1305—1312).—*Ethyl hydrogen lutidinecarboxylate*,

$$COOH\cdot C_5NHMe_2\cdot COOEt,$$

is obtained by treating the normal ethyl salt with alcoholic potash

solution, and afterwards boiling off most of the alcohol. Water is added, which precipitates much unchanged ethyl salt; it is then filtered, treated with hydrochloric acid, and evaporated to dryness. The monethyl salt is extracted with absolute alcohol. It forms slender, lustrous needles, sparingly soluble in cold water, and melts at 131°. The *hydrochloride* (with 2 mols. H_2O) forms small, lustrous prisms; it is very readily soluble; when the hydrogen ethyl salt is heated, it gives off carbonic anhydride and yields *ethyl lutidinecarboxylate*, boiling at about 240°.

Lutidinecarboxylic acid (2 : 6-dimethylnicotinic acid),

$$C_5NH_2Me_2{\cdot}COOH,$$

is obtained by heating the dicarboxylic acid (15 grams at a time) in a stream of hydrogen; the product is distilled with steam to separate it from the lutidine formed at the same time, and is purified by means of the hydrochloride. It crystallises with $\frac{1}{2}$ mol. H_2O in slender needles, melting at 160°. The *silver salt* and the *platinochloride* (with 2 mols. H_2O) are described.

2 : 5 : 6-*Pyridinetricarboxylic acid*, $C_5NH_2(COOH)_3$, is obtained by oxidising lutidinecarboxylic acid hydrochloride with potassium permanganate. It forms thin plates (with 2 mols. H_2O), very readily soluble; it melts a little above 100°, begins to give off gas at 130°, and decomposes completely at 240°. The *normal calcium salt*,

$$(C_8NH_2O_6)_2Ca_3 + 4H_2O,$$

the *lead salt* (with 5 mols. H_2O), and a *potassium salt*, $C_{24}H_{14}NO_{18}K + 5H_2O$, are described. When the latter is heated, it quickly loses 29 per cent. of its weight, and then remains constant at 160°; the weight lost corresponds nearly with the weight of the water of crystallisation, together with that of 3 mols. of carbonic anhydride. The potassium salt so obtained yielded an acid having all the properties of Weidel's isocinchomeronic acid (this vol., p. 477); the formation of this acid as described confirms the constitution [2 : 5] previously ascribed to it. N. H. M.

Phenyldihydroquinolylmethane. By A. Einhorn (*Ber.*, **19**, 1243 — 1244). — *Phenyldihydroquinolylmethane*, $CHPh(C_9NH_{10})_2$, is obtained by heating 10 grams of hydroquinoline, 4 grams of benzaldehyde, and 10 grams of zinc chloride, dissolved in absolute alcohol, at 100° for about 50 minutes. The product is poured into water; it is then purified by conversion into the hydrochloride. This is afterwards treated with alkali, and the free base dissolved in benzene and precipitated by adding light petroleum. It forms microscopic sulphur-coloured crystals, which melt at 152—153°. It has all the properties of a leuco-base. When the substance dissolved in alcoholic solution of hydrogen chloride is oxidised with ferric chloride, it yields a green dye.

Paranitrophenyldiquinolylmethane is obtained in a similar manner from nitrobenzaldehyde. It is a yellow substance, melting at 177°, and yields a green dye when oxidised; but if first reduced with zinc-dust and alcoholic hydrochloric acid, and then oxidised, a violet dye is obtained. N. H. M.

Quinolyl-α-hydroxypropionic Acid. By A. Einhorn (*Ber.*, **19**, 904—911; comp. this vol., pp. 264, 265, and 370).—*Trichlor-α-hydroxypropylquinoline*, $C_9NH_6{\cdot}CH_2{\cdot}CH(OH){\cdot}CCl_3$, is best prepared by heating 20 grams of quinaldine with 21 grams of chloral and about 1 gram of zinc chloride on a water-bath. A rise of temperature takes place, and in about an hour the whole solidifies to a crystalline mass. The yield of crude substance is 23—25 grams. It can be crystallised from absolute alcohol; it melts at 148°.

Quinolyl-α-hydroxypropionic acid, $C_9NH_6{\cdot}CH_2{\cdot}CH(OH){\cdot}COOH$, is obtained by dissolving 10 grams of the chlorine-derivative in 35 grams of absolute alcohol; 40 grams of water are then added, which precipitates the substance in a very finely divided state. The whole is warmed and 35 grams of a 23 per cent. solution of caustic soda are added. The reaction is violent and is completed in 5—10 minutes. The product is evaporated or cooled down and filtered from the orange-coloured sodium salt. The latter crystallises from water in long, lustrous, prismatic needles (with 3 mols. H_2O). When dried or when crystallised from absolute alcohol, it loses water and becomes yellow. The free acid forms splendid yellowish-red crystals (with 1 mol. H_2O), which melt at 123—125° with decomposition. The acid cannot be obtained anhydrous. When exposed to air, it changes to a colourless substance without taste. The mother-liquor from the sodium salt, mentioned above, yielded 1—2 grams of quinolylacrylic acid.

Quinolylacetaldehyde, $C_9NH_6{\cdot}CH_2{\cdot}CHO$, was prepared as previously described; it melts at 103—104°. It can also be obtained by boiling quinolyl-α-hydroxypropionic acid in benzene. The *picrate* forms sulphur-coloured crystals, which melt at 212°.

The substance previously obtained, to which the formula $C_{12}H_{11}NO_3$ was ascribed, could not again be prepared. It is probably a mixture of the compounds $C_{12}H_{13}NO_4$ and $C_{12}H_9NO_2$. N. H. M.

Tetramethylquinoline. By J. Levin and P. Riehm (*Ber.*, **19**, 1394—1395).—By the action of acetone on metaxylidine, a tetramethylquinoline is obtained together with methane and water. The base forms well-defined, tabular crystals, which melt at 84°, and boil without decomposition at 284—285° (uncorr.); it possesses a peculiar aromatic odour. Solution of its salts show the fluorescence characteristic of quinoline-derivatives; the *acid sulphate*, $C_{13}H_{15}N,H_2SO_4$, crystallises in needles very soluble in water; the *acid chromate* in dark orange-yellow needles, sparingly soluble; the *hydrochloride* in white needles; and the *platinochloride* is a golden, sparingly soluble precipitate. As regards the orientation of the methyl-group, the two methyl-groups in the pyridine nucleus are in the 2′ : 4′ positions, but that of the methyl-groups in the benzene nucleus is uncertain.

V. H. V.

Derivatives of α-Phenylquinoline. By O. Doebner and W. Miller (*Ber.*, **19**, 1194—1200).—When a solution of α-phenylquinoline in sulphuric acid is oxidised with potassium permanganate by

Claus and Nicolaysen's method for the oxidation of phenylacridine (this vol., p. 68), benzoylanthranilic acid is formed.

α-Phenylquinoline picrate, $C_{15}H_{11}N + C_6H_3N_3O_7$, crystallises from hot alcohol in yellow scales. The methiodide, $C_{15}H_{11}N,MeI$ is formed by heating α-phenylquinoline with methyl iodide on the water-bath in a reflux apparatus for several hours; it crystallises from alcohol in thick orange-coloured prisms, melts at 197°, and is sparingly soluble in water, but insoluble in ether.

Tetrahydro-α-phenylquinoline, $C_{15}H_{15}N$, may be prepared by heating α-phenylquinoline with tin and hydrochloric acid for several hours, adding excess of soda to the resulting liquid, and extracting with ether; it forms a colourless, viscous oil insoluble in water, but dissolving readily in ether or hot alcohol; it boils at 341—344°. The *hydrochloride*, $C_{15}H_{15}NHCl$, crystallises from alcohol in slender needles, and is very sparingly soluble in water. The *platinochloride* forms a yellow precipitate which rapidly decomposes, turning brown.

Nitrosotetrahydro-α-phenylquinoline is obtained by shaking up tetrahydro-α-phenylquinoline hydrochloride with the theoretical amount of sodium nitrite in aqueous solution, and extracting with ether; it forms a thick, yellow oil which cannot be solidified by cooling.

In the preparation of α-phenylquinoline from aniline, cinnamic aldehyde, and hydrochloric acid, the chloride of an ammonium base, $C_{17}N_{16}NCl + 2H_2O$, is obtained; it forms colourless needles, is readily soluble in alcohol or water, but insoluble in ether; the chlorine is not removed by boiling with ammonia, but concentrated fixed alkalis form resinous compounds.

The *platinochloride* and other salts were prepared. This base closely resembles the compound of α-phenylquinoline with ethyl-chloride, and possibly is identical with that compound. A. P.

Quinoxalines. By J. Plöchl (*Ber.*, **19**, 895—896).—A reply to Hinsberg (this vol., p. 561).

Paramidoquinoxaline. By O. Hinsberg (*Ber.*, **19**, 1253—1256). —*Paramidoquinoxaline*, $NH_2{\cdot}C_6H_4{<}\begin{matrix}N:CH\\N:CH\end{matrix}{>}$, is prepared by adding magnesia to crude phenylenetriamine hydrochloride dissolved in water; it is then warmed, and treated with a slight excess of the sodium hydrogen sulphite-compound of glyoxal. The product is made strongly alkaline and extracted with chloroform; it is then purified by crystallisation from ether, from which it separates in yellow needles melting at 158—159°. It is readily soluble in water, chloroform, and alcohol, less soluble in ether and benzene. The ethereal solution has a yellowish-green fluorescence; the solution in concentrated mineral acids has an intense violet colour, which changes to a brownish-red when the solution is diluted. The *hydrochloride* forms brown plates which decompose at 215°. The *platinochloride* crystallises in brick-red needles; the *sulphate* forms a sparingly soluble, brick-red, crystalline powder. An aqueous solution of amidoquinoxaline gives yellow precipitates with silver nitrate and mercuric chloride, soluble in nitric and hydrochloric acids. N. H. M.

Cantharidin. By J. Piccard (*Ber.*, **19**, 1404—1407).—Cantharic acid is prepared by rubbing cantharidin in a mortar with ether, filtering, and drying; the product is then heated with four times its weight of hydriodic acid (sp. gr. = 1·96) at 100° for 2½ hours. The contents of the bottle are distributed into several dishes, and evaporated as quickly as possible, and the brown residue at once extracted with a little cold alcohol, which dissolves everything but the unchanged cantharidin. The alcoholic solution is evaporated down; in 2—3 weeks a crystalline mass is formed, consisting of the compound $C_{10}H_{12}I_2O_3$; the filtrate contains cantharic acid.

When cantharic acid or cantharidin is heated with water at 300°, it yields cantharene and carbonic anhydride.

Cantharic acid reacts very readily with phosphorus pentachloride, and yields a liquid product soluble in ether, alcohol, and benzene; from this two crystalline substances were obtained by the action of ammonia on ethereal and alcoholic solutions respectively.

N. H. M.

Cantharidin. By B. Homolka (*Ber.*, **19**, 1082—1089).—Although this substance has been the subject of very many investigations, and the determination of its vapour-density by Piccard proved its molecule to have the formula $C_{10}H_{12}O_4$, little is known as to its constitution. Dragendorff and Masing showed that when boiled with alkalis, it gradually dissolved, and formed a salt, $C_{10}H_{12}O_5M_2$, but stated that on the addition of acids cantharidin was reprecipitated unchanged in the form of needles. The author finds that, although this latter statement is true when an acid is added to the *hot* alkaline solution, no precipitate is formed in a *cold* weak solution. When this clear solution is heated to 60—70°, however, cantharidin is at once precipitated. There is thus little doubt that the free *cantharidic acid*, $C_{10}H_{12}O_5$, was present in the cold solution, but, owing to the readiness with which it gives up water, and forms its anhydride, cantharidin, the author was unable to isolate the acid. *Silver cantharidate* forms a precipitate, $C_{10}H_{12}O_5Ag_2 + H_2O$; *methyl cantharidate*, $C_{10}H_{12}O_5Me_2$, prepared from the silver salt, crystallises in flat prisms easily soluble in alcohol, boiling ether, and water; it melts at 91°. With hydroxylamine, cantharidin yields *cantharidoxime*, $C_{10}H_{12}O_3(N{\cdot}OH)$, crystallising in stellate needles or prisms, soluble in ether, alcohol, and warm water; it melts at 166°. When heated with hydrochloric acid at 150°, it is resolved into its constituents. The author also, by the action of free hydroxylamine on sodium cantharidate, obtained the *sodium* and *lead* salts of a *cantharidoximic acid*, but was unable to obtain the free acid, as this is at once converted into its anhydride, cantharidoxime. Cantharidoxime dissolves unchanged in soda, but on boiling the solution ammonia is evolved. The *silver-derivative*, $C_{10}H_{12}O_4NAg$, crystallises in quadratic prisms; the *methyl ether* forms large, colourless prisms melting at 134°.

Cantharic acid (Piccard, Abstr., 1878, 233; 1879, 270, and preceding Abstract) yields a white *silver salt*, and a *methyl salt* boiling at 210—220° under 50 mm. pressure. With hydroxylamine, this acid forms *cantharoximic acid*, $C_{10}H_{13}O_4N$ (isomeric with cantharidoxime), crystallising in colourless, quadratic scales, which melt with decompo-

sition between 175 and 180°. When heated with hydrochloric acid at 150°, cantharic acid and hydroxylamine are re-formed, together with a small quantity of an oily product having the properties of an aldehyde.

When cantharic acid is heated at 140—150° with dimethylaniline and zinc chloride, carbonic anhydride is evolved, and a leuco-base obtained which forms a colourless crystalline mass having basic properties, and becoming green on contact with the air. Its *platinochloride*, $C_{22}H_{32}ON_2,H_2PtCl_6$, forms orange crystals. When oxidised, the base forms colouring matters, the colour varying with the oxidising agent employed. Thus braunite and dilute sulphuric acid produce a green, chloranil or arsenic acid in acid solutions a violet colour. Such a condensation of an aromatic carboxylic acid with dimethylaniline, accompanied by the evolution of carbonic anhydride, only takes place (Abstr., 1885, 758) when the acid contains the α-ketone-group, CO·COOH.

From the results of his experiments, the author concludes that both cantharidic and cantharic acids must contain this group, and their formulæ must therefore be $C_8H_{13}O_2{\cdot}CO{\cdot}COOH$ and $C_8H_{11}O{\cdot}CO{\cdot}COOH$ respectively. L. T. T.

Hopeïne. By W. Williamson (*Chem. Zeit.*, **10**, 491—492).—The author's results confirm those of Ladenburg (this vol., p. 563), and the alkaloïd, which is unlike morphine, is now regarded as hopeïne. It crystallises from aqueous alcohol in needles, melts below 100°, and sublimes partially below 160°. Pure hopeïne is slightly lævorotatory, and in dilute solutions is precipitated by alkalis, platinic, auric, and mercuric chlorides, and by picric and tannic acids. D. A. L.

Pilocarpine. By E. Hardy and G. Calmels (*Compt. rend.*, **102**, 1116—1119).—The authors have analysed the following compounds of pilocarpine: the nitrate, $C_{11}H_{16}N_2O_2,HNO_3$, which forms rhombic lamellæ, very soluble in water but less soluble in alcohol; the platinochloride, $(C_{11}H_{16}N_2O_2)_2,H_2PtCl_6$, which forms somewhat soluble quadratic prisms and lamellæ; the modified platinochloride, $(C_{11}H_{16}N_2O_2)_2PtCl_4$, a very soluble, crystalline, yellow powder; the aurochloride, $C_{11}H_{16}N_2O_2AuCl_3$, formed in slender needles when the pilocarpine is in excess; the aurochloride, $C_{11}H_{16}N_2O_2,2AuCl_3$, obtained in microscopic needles when the auric chloride is in excess. Both these compounds form viscous oils when heated in presence of water, and combine with only one equivalent of hydrogen chloride. The acid aurochloride, $C_{11}H_{16}N_2O_2,HAuCl_4$, obtained in needles by adding a limited quantity of auric chloride to a solution containing free hydrochloric acid; the acid diaurochloride, $C_{11}H_{16}N_2O_2,2HAuCl_4$, obtained in needles or right rectangular prisms by adding excess of auric chloride in presence of hydrochloric acid; the mercurochlorides, which crystallise in slender needles and are very soluble in acids; and the hydrochloride, which forms a gummy mass. Pilocarpine itself is a viscous substance, very soluble in alcohol and water, slightly soluble in cold ether or chloroform, more soluble on heating, and readily soluble in ether or chloroform mixed with alcohol. Pilocarpine does not act on carbonates, but with alkaline hydroxides it forms compounds

which are decomposed by carbonic acid. These facts point to the presence of an internal anhydride. Pilocarpic acid does not exist in the free state. The copper salt, $(C_{11}H_{17}N_2O_3)_2Cu$, is a slightly soluble green powder, and the silver salt forms a curdy precipitate. Free pilocarpine forms with silver nitrate two compounds,

$$AgNO_3,C_{11}H_{16}N_2O_2,$$

and $(AgNO_3)_2,C_{11}H_{16}N_2O_2$, which crystallises in needles. The constitution of pilocarpine is represented by the formula

$$C_5H_4N^{\beta}\cdot CMe<\begin{matrix}-CO-\\ NMe_3\end{matrix}>O.$$

Pilocarpidine.—The substance produced by the action of nitric or hydrochloric acid on pilocarpine or by boiling pilocarpine or its salts with water in presence of air, is pilocarpidine,

$$C_8H_4N^{\beta}\cdot CMe(NMe_2)\cdot COOH.$$

Its salts are similar to those of pilocarpine; they are gummy substances decomposed by carbonic anhydride, soluble in water and alcohol of 90°, but insoluble in absolute alcohol if they are dry. The copper salt is green, the silver salt crystallises in a mass of small needles. The hydrochloride is soluble in water and crystallises badly from an acid solution; it is a gummy substance which crystallises slowly from alcohol in scales with a prismatic structure. The aurochoride, $C_{10}H_{14}N_2O_2,HAuCl_4$, is obtained in right rectangular prisms by adding pilocarpidine hydrochloride gradually to an acid solution of auric chloride, and allowing the liquid to evaporate spontaneously. In solutions containing no free acid, the aurochloride, $C_{10}H_{14}N_2O_2,AuCl_3$, is formed. The platinochloride, $(C_{10}H_{14}N_2O_2)_2,H_2PtCl_6 + 2H_2O$, is formed in lamellæ by adding the hydrochloride to an excess of platinum chloride solution. If these crystals are dissolved in a large quantity of cold water and allowed to recrystallise in the cold, the platinochloride separates in large, yellow lamellæ similar to those of naphthalene. If crystallisation takes place in a warm solution, small red prismatic crystals of the composition $(C_{10}H_{14}N_2O_2)_2,H_2PtCl_6 + H_2O$ separate. This second modification is also obtained by heating the dehydrated salt. C. H. B.

A New Nitrogenous Principle of the Germinated Seeds of Lupinus Luteus. By E. Schulze and E. Steiger (*Ber.*, **19**, 1177—1180).—The etiolated germinated cotyledons of *Lupinus* contain a nitrogenous base somewhat similar in its properties to creatinine. It may be most conveniently isolated by precipitating the aqueous extract with tannin and lead acetate, acidifying the filtrate with sulphuric acid, filtering, and adding phosphotungstic acid to the filtrate, when a copious white precipitate is formed; this is washed and mixed with milk of lime, and the filtered solution freed from calcium by passing carbonic anhydride; the solution is then filtered, neutralised with nitric acid, and concentrated to a syrup, when the nitrate of the base, to which the authors give the name of *arginine*,

$C_6H_{14}N_4O_2,HNO_3 + \frac{1}{2}H_2O$, crystallises out on cooling in groups of slender needles; on drying at 100°, it loses water and forms a chalk-like mass. It is tolerably soluble in cold, and readily in hot water. The aqueous solution gives a yellow crystalline precipitate with picric acid and on the addition of mercuric nitrate or chloride and then of an alkali, a voluminous white precipitate is formed. On heating the aqueous solution of the nitrate with cupric hydroxide, a blue solution is formed, which on cooling yields fine, dark blue prisms of a compound of arginine with cupric nitrate, $2(C_6H_{14}N_4O_2)Cu(NO_3)_2 + 3H_2O$; on drying at 100° it loses its water of crystallisation. The free base, $C_6H_{14}N_4O_2$, may be obtained by adding phosphotungstic acid to an aqueous solution of arginine nitrate, and treating the white precipitate formed with milk of lime, filtering and concentrating the solution, when it crystallises out; it readily absorbs carbonic anhydride. *Arginine hydrochloride*, $C_6H_{14}N_4O_2,HCl$, forms large crystals; it also forms a readily soluble crystalline compound with cupric hydroxide.

Lupine seeds which have germinated for 2 to 3 weeks yield 3 to 4 per cent. of arginine hydrochloride. A. P.

Decomposition Products of Hæmoglobin. By F. Hoppe-Seyler (*Zeit. physiol. Chem.*, **10**, 331—335).—The author corrects certain statements, especially some having regard to priority of discovery, recently made by Nencki and Sieber (*Arch. experim. Path. u. Pharmacol.*, **20**, 325—346). He regards the parahæmoglobin crystals of these authors as a coagulation product of oxyhæmoglobin, brought about by the action of alcohol; these crystals do not show double refraction, and by decomposition in the absence of oxygen yield hæmochromogen and not hæmoglobin. W. D. H.

Physiological Chemistry.

The Diastatic Ferment in Saliva. By H. Goldschmidt (*Zeit. physiol. Chem.*, **10**, 273—301).—The research was directed to ascertain whether the ferment in saliva is preformed in the salivary glands or not. The parotid saliva of the horse was used. This saliva, collected without antiseptic precautions, is not always immediately active, and in some cases although not in all, it becomes so after a short time. When collected with strict antiseptic precautions, it is perfectly clear and remains so for many days, or at most is only slightly cloudy; whereas the onset of cloudiness (due to the evolution of carbonic acid and the precipitation of carbonate of lime) is very rapid without such precautions. Antiseptic saliva is always completely inactive on sterilised starch, but resumes its activity when exposed to the atmosphere. The conclusion is drawn that an active ferment is not formed in the glands.

The alcoholic precipitate of such saliva, however, is found to possess diastatic properties.

The passage of a stream of carbonic anhydride through cloudy (not antiseptic) saliva does not destroy the ferment, but hinders its action to a small extent. The change which the air works in saliva is also not dependent on the oxygen, but more probably on the germs found in the atmosphere. Culture experiments performed with extracts of the salivary glands (made with glycerol and with weak carbolic acid), with pieces of the glands removed antiseptically, and with the parotid saliva of the horse, showed that various forms of micrococcus, bacterium, and bacillus developed; but these had no diastatic properties. A variety of mould which developed in a few cultivations was found to possess diastatic properties; this may, however, be obtained from the atmosphere without any admixture of saliva or salivary glands. This mould is most active in the earlier stages of its growth, and is probably identical with *Penicillium glaucum*.

Not only is sugar formed from starch by the action of saliva on it, but also a certain amount of fatty acids, especially lactic acid. The amount of sugar formed varies with the amount of saliva employed, but not proportionally. The formation of lactic acid hinders the action of the diastatic ferment. Considerable variations in the proportional amount of sugar and lactic acid is accounted for by supposing that under certain circumstances the lactic acid may break up into butyric acid, carbonic anhydride, and hydrogen; these products being volatile pass off and so allow more starch to be subjected to saccharification. W. D. H.

Sugar as an Addition to Cattle Food. By Holdefleiss (*Bied. Centr.*, 1886, 303—305).—The low price of sugar has caused many experiments to be made as to its value in cattle feeding; in previous experiments, its theoretical nutritive value was calculated, and it was mixed with the food in regular proportions; in the present experiment, it was given as an extra ration or condiment.

Thirteen oxen were the animals chosen for experiment; they were all fed in the same way, except that two of them daily received a ration of 1 kilo. of sugar extra; these animals showed a considerably larger increase of live-weight than the other eleven—amongst the latter there were great differences in fattening capacity. The sugar-fed oxen received each, during the whole period, 112·5 kilos. of raw sugar, from which the author calculates that 50 kilos. of sugar is capable of producing an increase of 15·75 kilos. live-weight, leaving a large money profit. The butchers who slaughtered the animals pronounced the meat of all the animals equally good.

With young cattle, the results were not so satisfactory; they did not eat freely, and suffered so much from scour that the supply of sugar had to be stopped. J. F.

Physiology of Digestion. By C. A. Ewald and J. Boas (*Bied. Centr.*, 1886, 354).—The authors found on examination of the contents of the stomach of a person subject to vomiting, that after a mixed meal of meat and carbohydrates, lactic acid was found in the

filtrate for from the first 10 to 100 minutes, but that when pure boiled albumin was eaten, no lactic acid was found; then follows a period when both lactic and hydrochloric acids were present; afterwards a third period in which the latter only was observed.

The lactic acid is either a product of the fermentation of the carbohydrates or is dissolved out of the meat. The hydrochloric acid can only be considered as a product of the secretions of the glands of the stomach.

The peptonising commences immediately after taking food, and appears to be commenced by the lactic acid, when the diet is a mixed one; the curves of the peptone and hydrochloric acid are identical, and reach their highest point about the middle of the digestive process, and a considerable time previous to the disappearance of the contents of the stomach. J. F.

Assimilation of Food. By F. Hofmeister (*Bied. Centr.*, 1886, 354).—The author's experiments on digestion have led him to the conclusion that the mucous membrane of the stomach and intestines contains larger quantities of peptone than the blood, it having been found after four hours' digestion; the lining of the intestinal canal has not only the power of secreting peptone, but of decomposing it, so that it no longer responds to the usual reactions. The part so changed passes at once into the tissues of the body; the unaltered portion passes into the blood where it does not exist in a free state, but in combination with the cells. J. F.

Does Cellulose Economise the Decomposition of Proteïd in the Nutrition of Herbivora? By H. Weiske, B. Schulze, and E. Flechsig (*Zeit. f. Biol.*, **22**, 373—403).—It has long been known that cellulose from various sources is digested in considerable quantities by many animals. Hoppe-Seyler, Popoff, and Tappeiner proved that this so-called digestion is due to a special organised ferment, and is, therefore, analogous to fermentative processes outside the body. By the action of this organised ferment, cellulose is decomposed, partly into carbonic anhydride and marsh-gas, partly into acetic and butyric acids. Ellenberger and Hofmeister have shown that cellulose, when submitted to artificial digestion, does not give rise to sugar, or, at most, only traces thereof.

The truth of the generally accepted theory that cellulose in the nutrition of Herbivora is equal to starch as an economiser of proteïd, therefore appeared questionable.

The plan of the present research was to determine the economising power of equivalent quantities of digestible cellulose and starch on the proteïd decomposition during a rich nitrogenous diet. The research was divided into three periods. During the first period, the experimental animal, a wether sheep, was fed for 7 or 8 days on a diet of beans. In the second and third periods cellulose and starch were respectively added to this diet.

The following are the daily averages of the nitrogen intake and output during the three periods:—

	Period I. Beans.	Period II. Beans and oat-chaff.	Period III. Beans and starch.
Nitrogen taken in food	22·62 grams.	24·82 grams.	22·75 grams.
Nitrogen eliminated in fæces	2·11 ,,	5·24 ,,	2·72 ,,
Nitrogen eliminated in urine	20·93 ,,	16·82 ,,	14·94 ,,
Difference....	0·42 ,,	+ 2·76 ,,	+ 5·09 ,,

The cellulose diet consisted of 500 grams of oat-chaff containing 88 grams of digestible cellulose and 82 grams of nitrogen-free extractives.

Further research showed that the plus 2·76 grams of nitrogen in the second or cellulose period could be accounted for by the 82 grams of nitrogen-free extractives, which consist in part of starch and other allied carbohydrates. Cellulose, therefore, does not, as hitherto supposed, economise the decomposition of proteïds.

W. V. Knierem (Abstr., 1885, 916) from his experiments on rabbits came to precisely the opposite conclusion. The author has repeated these experiments, and finds that cellulose produced no economy; in fact, in one instance, even an increased decomposition.

J. P. L.

Pancreatic Digestion. By A. Hirschler (*Zeit. physiol. Chem.*, **10**, 302—305).—In addition to the products of the pancreatic digestion of fibrin, a small quantity of ammonia is also formed. This may be detected and estimated by the platinic chloride method in the distillate from a digestion in which no putrefaction has occurred.

W. D. H.

Influence of Carbohydrates and other Substances on the Putrefaction of Proteïds. By A. Hirschler (*Zeit. physiol. Chem.*, **10**, 306—317).—Putrefaction readily occurs in the pancreatic digestion of proteïds, indole, skatole, phenol, and oxyacids being formed. The addition of small quantities of (8 grams to 250 grams of meat) sugar, starch, dextrin, glycerol, and lactic acid, entirely prevents the formation of these substances in artificial digestion experiments. It is supposed that the fungi which develop in such experiments decompose these substances more readily than they do albuminous materials, and hence the latter escape putrefactive decomposition. Fat has on the contrary no such action. This has a practical bearing in view of preventing putrefaction in the alimentary canal; but by means of experiments, which consisted in feeding dogs on a flesh diet mixed with sugar, starch, and glycerol respectively, the following result was obtained: the formation of the putrefaction products of proteïds was lessened but not completely prevented; this is probably because sugar, starch, &c., are substances which are very rapidly absorbed and so removed from the alimentary canal. W. D. H.

Ethereal Hydrogen Sulphates in Urine. By V. Morax (*Zeit. physiol. Chem.*, **10**, 318—325).—The relation of the sulphuric acid to

the ethereal hydrogen sulphates in urine is taken as a measure of the amount of putrefactive decomposition of albumin in the alimentary canal.

In a dog, the average of five experiments showed that the proportion of sulphuric acid to ethereal hydrogen sulphates was normally 8 : 1. When 5 grams of iodoform was given daily, the proportion rose to 35 : 1, showing that iodoform is an antiseptic in the alimentary canal. Bismuth subnitrate has no such effect. Calomel diminishes the amount of ethereal hydrogen sulphates in the urine only, when at the same time the contents of the alimentary canal are rapidly removed by severe diarrhœa. In the dog, castor oil, croton oil, and magnesium chloride do not act as laxatives, and their effects were not investigated.

In man, castor oil and calomel produce no appreciable diminution in the amount of ethereal hydrogen sulphates in the urine. The difference in the action of calomel in man and the dog is probably due to the fact that it is impossible to administer such large doses of calomel to human beings as can be given to dogs experimentally.

W. D. H.

Aromatic Substances in the Animal Organism. E. Salkowski (*Zeit. physiol. Chem.*, **10**, 265—272).—The author comments on recent researches on the occurrence of aromatic compounds in the urine of starving animals, which therefore could not have been formed by putrefactive processes in the alimentary canal; and discusses the question whether they are formed in the tissues by bacteria, or by a soluble ferment independently of the growth of such organisms.

W. D. H.

Action of Cacodylic Acid on the Animal Economy. By J. Marshall and W. D. Green (*Amer. Chem. J.*, **8**, 128—138).—Several experimenters have found that cacodylic acid has no poisonous properties, but Lebahn found that rabbits died in from 1 to 25 days after injection of quantities of cacodylic acid up to 2·3 grams. A commercial sample of cacodylic acid was found to contain arsenious anhydride as impurity, and as Lebahn does not refer to the purity of the reagent he employed, it is possible that his results are vitiated from this cause. Cacodylic acid of ascertained purity was given in small doses amounting to 1 to 3 grams without any permanent effects; salivation, vomiting, and defectation, being the temporary effects. Injections of 2 to 3 grams produced the same effects as above, except in the case of one small dog that died after an injection of 3 grams. The general effects produced by cacodylic acid and arsenious anhydride are therefore similar, but those of cacodylic acid quickly pass away.

H. B.

Chemistry of Vegetable Physiology and Agriculture.

Biological and Chemical Properties of Micro-organisms, and the Formation of Ptomaïnes by Cholera Bacilli. By A. Poehl (*Ber.*, **19**, 1159—1165).—In cases where the secretions of the stomach do not possess the antiseptic action which Bienstock has shown to be normal, the fæces contain large numbers of micro-organisms capable of decomposing albumin. In experiments on the patients of the Obuchow Hospital, St. Petersburgh, many micro-organisms which bore no spores, and especially coccus, were detected, besides the bacilli described by Bienstock.

Bacteria act at once both as reducing and oxidising agents, the formation of ptomaïnes being due to the decomposition and simultaneous reduction of albuminoïds. In order to render readily apparent the presence or absence of this reducing action in cultivations of micro-organisms, the author has mixed with Koch's gelatin about 0·05 per cent. of ferric chloride and potassium ferricyanide and, after sterilisation, inoculated the mixture with various organisms, any reducing agent was then at once shown by the formation of Prussian blue, in some cases a change took place in from 12—24 hours, in some a much longer time was required, whilst in others the blue did not appear at all. In all cases it was noticeable that the reducing action as shown by the blue coloration, commenced at a distance of from 4—8 mm. from the surface, the air appearing to retard the formation of the ptomaïnes.

In conducting experiments with cultivations in which ferric chloride and potassium ferricyanide are present, some precautions are necessary. The addition of the ferric chloride must be made after sterilisation of the gelatin and when it is almost set, as on heating it in the presence of ferric chloride iron albuminate is formed, and the delicacy of the reaction is much interfered with. In all cases the cultivations must be protected from the direct action of light so as to avoid decomposition of the ferricyanide. In some cases the gelatin, after the addition of the ferric chloride and potassium ferricyanide, must be rendered slightly alkaline, as some organisms are only capable of reproduction in alkaline media; after a suitable time the presence or absence of reducing action is determined by the addition of hydrochloric acid. Another class of micro-organisms such as the bacilli from fæces, are only reproduced at a temperature at which Koch's gelatin is fluid, the author therefore under these circumstances employs a mixture of equal parts of Koch's and Agar-agar gelatins.

From experiments conducted in the above manner, the author finds that the *Comma* and *Typhus bacilli*, *Strepto coccus*, many micro-organisms from the fæces, from sputa, water of the Neva, and from the St. Petersburgh sewage, exhibit a reducing action, whilst some micro-organisms, such as the *Bacillus subtilis*, give no sign of any reducing action even after cultivation for a week; in no case when the organism rendered the gelatin fluid by its reproduction, was any reducing action observable.

Micro-organisms which are reproduced in alkaline media, such as the *Cholera bacillus*, yield after the addition of hydrochloric acid a red colouring matter which is soluble in amyl alcohol, but insoluble in chloroform, in its absorption-spectrum and general properties it much resembles the derivative of skatole, obtained from pathological urine, and described by Plósz (Abstr., 1884, 1059).

The author was unable to obtain any specimens of the bacillus *Cholera nostras* to examine by his method, but some years ago he examined its action on syntonin, and was unable to detect the formation of any ptomaïnes, although the syntonin was almost completely peptonised in 24 hours: he therefore considers that the difference in the action of the bacilli *Cholera asiatica* and *Cholera nostras* is due to the fact that the former has a reducing action, absorbing oxygen and forming poisonous ptomaïnes, whilst the latter does not form ptomaïnes and requires a much smaller amount of oxygen. On these grounds, in cases of *Cholera asiatica*, the author proposes the employment of remedies which will supply oxygen to the bacilli, thus preventing the reduction of the albuminoïds and consequent formation of ptomaïnes.

By cultivating the bacillus of *Cholera asiatica* in slightly alkaline gelatin containing ferric chloride and potassium ferricyanide, Prussian blue is produced and the gelatin is not rendered fluid, but if a fresh portion of gelatin be inoculated with the result of this first cultivation it rapidly becomes fluid, the action of the original bacillus having evidently been much altered, and the author considers it possible that he has by this means transformed the bacillus of *Cholera asiatica* into that of *Cholera nostras*. A. P.

Acetous Fermentation. By A. Romegialli (*Gazzetta*, **16**, 73—101).—In this paper, a series of comparative experiments are described, which were made with a view of determining the best cultivation liquid, other than diluted wine, for *Mycoderma aceti*. A number of liquids were made up in imitation of wine extracts, and their suitability compared by ascertaining the weight of the pellicle of ferment and of the acetic acid formed, other conditions remaining the same. From the results it seems that the growth of ferment is increased by the presence of glycerol, and of succinic and malic acids, of which the first is the most readily assimilated; secondly, asparagine is more favourable than albumin, whilst ammonium chloride and phosphate are not convenient media for furnishing the requisite nitrogen. The presence of sulphur, silica, and iron are useful, if not indispensable to the ferment.

The *Mycoderma aceti* (?) contains 71·3 per cent. of a substance showing all the reactions of cellulose (comp. Brown, Trans., 1886, 434), the remainder consists of albumin, fatty substance, and ash (4·4 per cent.), the last consisting of chlorine, silicic, phosphoric, sulphuric, and carbonic acids, combined with potash, soda, lime, magnesia, and ferric oxide.

It is also shown that sulphurous acid is a better antiseptic against the acetic fermentation than salicylic acid. V. H. V.

Lactic Fermentation. By G. Marpmann (*Arch. Pharm.* [3], **24**, 243—256).—The author remarks on the very contradictory views still prevailing as to the nature of lactic fermentation. During the past summer he has investigated the micro-organisms of cow's milk in the neighbourhood of Göttingen, and has detected five seemingly new and different species, which more or less strongly induce lactic fermentation in cane-sugar as well as in milk. Coagulated milk filtered, mixed with 10 per cent. of pure gelatin, and carefully sterilised by means of heat, was employed for the cultivation, and the solution to be tested was brought into contact with it on glass plates. As the different organisms developed, they were employed to commence fresh growths, and by this process of selection pure cultivations were at length obtained. The action of these organisms on milk was then investigated quantitatively, but the results are not given. The author is still engaged on the subject. J. T.

Abnormal Secretion of Nitrogenous Substances by Yeasts and Moulds. By U. Gayon and E. Dubourg (*Compt. rend.*, **102**, 978—980).—When yeast is suspended in water, only a small quantity of nitrogenous matter passes into solution, and this is not coagulable by heat. If the water is replaced by concentrated solutions of such salts as potassium acetate, oxalate or iodide, sodium phosphate or sulphate, calcium chloride, magnesium sulphate, tartar emetic, &c., the liquid dissolves a considerable quantity of albuminoïds which are either partially coagulable by heat and acids or not coagulable at all. The total amount of albuminoïds dissolved, and the ratio between the coagulable and non-coagulable portions, depend on the nature of the saline solution. After the yeast has been treated with these solutions, it can still yield to water a considerable quantity of albuminoïds partly coagulable and partly non-coagulable. Many other soluble substances behave in the same way as the above salts. If yeast is previously treated with methyl, ethyl, propyl, or octyl alcohols, glycol, or glycerol, it yields to water coagulable albumin, but if treated with isopropyl alcohol, or butyl or isobutyl alcohol, it yields only non-coagulable albumin to water.

The yeast which has been deprived of its nitrogenous matter is greatly modified in appearance, dimensions, and vitality. Sometimes it is killed, but in many cases it revives easily when placed in saccharine musts. The abnormal secretion of nitrogenous substances under the influence of strong saline solutions is correlative with an increased production of soluble ferment. All the varieties of yeast which produce inversion behave in the same way, and give an abundant secretion of albumin and invertin or sucrase, but those which do not cause inversion behave quite differently, and yield no more albumin to saline solutions than to pure water. The same behaviour is observed in the case of inversive and non-inversive moulds.

It would seem, therefore, that the inversive power of a yeast or mould is intimately connected with the readiness with which its membrane permits the passage of albuminoïds. C. H. B.

Composition of the Wheat Germ; Presence of a New Sugar and of Allantoïn. By C. Richardson and C. A. Crampton (*Ber.*, **19**, 1180—1181).—Wheat germs contain an oil which may be readily dissolved out, is easily dried, and might be employed with advantage for technical purposes. After the extraction of the oil, hot alcohol (80 per cent.) readily extracts 15—18 per cent. of sugar; 80—90 per cent. of this is cane-sugar, the residue consists of a saccharoid which is strongly dextrorotatory, does not reduce Fehling's solution, and is not fermentable; yeast, however, converts it into a sugar which reduces Fehling's solution.

About $\frac{1}{2}$ per cent. of allantoïn was found in the nitrogenous constituents of the germs; a wax-like fat was also separated which is sparingly soluble in light petroleum, and cannot be saponified.

A. P.

Formation of Oxalic Acid in Vegetation. By Berthelot and André (*Compt. rend.*, **102**, 995—1001, 1043—1049).—The soluble and insoluble oxalic acid was estimated by the method previously described (Abstr., 1885, 1164). The plants selected and examined at various stages of their growth were *Rumex acetosa*, *Amarantus caudatus*, *Chenopodium quinoa*, and *Mesembrianthemum cristallinum*. The juice of the first is always acid, that of the second and third neutral or feebly acid, whilst that of the last is neutral in the early stages of growth but becomes acid as the plant develops. The plants also differ very considerably in the ratio between the soluble and insoluble oxalates which they contain.

Rumex acetosa.—The seed or dried fruit contains 0·05 per cent. of oxalic acid. In the early stage of growth (June 8th) the root contains 13·9 per cent. of oxalic acid, 5·1 per cent. being soluble and the remainder insoluble. The proportion of ash is 20·7 per cent., and some of the acid is in the free state. When the plant is in active vegetation (June 26th), the absolute quantity of oxalic acid has increased, but the relative proportion has diminished owing to the development of ligneous tissue and albuminoïds. The total proportion is about 10 per cent., and it is especially abundant in the leaves and limbs, and least abundant in the root, in which it is almost entirely insoluble owing to the proximity of the calcium compounds in the soil. In the limbs, about one half is in the insoluble condition. The actual acidity is below the total oxalic acid in the limbs, but is higher in the roots and petioles, and hence the latter contain some acid other than oxalic acid. The limbs contain soluble oxalates and soluble calcium salts in almost equivalent quantities, but these must either circulate in different vessels or exist in the form of ethereal salts or double salts. The existence of soluble oxalates and calcium salts in the same parts of a plant may in fact be explained in three ways. The oxalates may exist in the form of double salts of potassium, calcium, and magnesium, dissociable by water, or the formation of oxalic acid may take place in special vessels, or the oxalic acid may exist in the form of ethereal salts which are ultimately decomposed in contact with calcium compounds.

When the plant begins to fructify (September 27th), the absolute amount of oxalic acid has increased but in much lower proportion

than the increase of the whole plant, so that the percentage amount is only one-fourth of what it was at the early stage of growth. The decrease is most considerable in the roots and limbs. In the former, almost all the oxalic acid is in the insoluble form, whilst in the limbs and petioles the soluble oxalates preponderate. At the same time there is a diminution in the proportion of ash. The calcium is in excess of the oxalic acid in the root but in the petioles and stalks the reverse is the case. The limbs are rich in soluble oxalates and also in calcium salts.

The leaves of *R. acetosa* are very rich in nitrogenous substances. They are also the principal seat of the formation of oxalic acid, whereas nitrates undergo destruction in the leaves (*Ann. Chem. Phys.* [6], **8**, 41). It would seem therefore that the oxalic acid is a product of the incomplete reduction of carbonic acid. If, however, the ratio of oxygen expired to carbonic anhydride absorbed remains constant, the production of oxalic acid in this way would require the simultaneous production of some highly hydrogenised compound as a compensating reaction. Such hydrogenised compounds are found in the albuminoids which are so abundant in the leaves.

Amarantus caudatus.—This plant contains a considerable proportion of nitrates (*loc. cit.*) and the oxalic acid is mainly in an insoluble form. At the commencement of inflorescence (June 18th), the percentage of oxalic acid was 5·86 or about half that found in *R. acetosa*. The nitrates are found chiefly in the stalks whilst the oxalates are most abundant in the leaves and flowers. As inflorescence progresses (July 26th), the amount of oxalic acid increases in proportion to the growth of the plant but remains almost entirely in the insoluble form. When inflorescence was fully developed (September 17th), the total weight of the plant had increased sixfold, whilst the amount of oxalic acid remained the same, still in the insoluble form and existing in greatest abundance in the leaves. It would seem therefore that the formation of oxalic acid takes place principally during the earlier stages of the plant's growth, and ceases during the period of inflorescence.

Chenopodium quinoa yields a neutral juice which is almost free from nitrates, but contains a relatively large proportion of soluble oxalates. In the early stage of growth (May 18th), the percentage of oxalic acid was 3·9, and the bases in the ash (25·6 per cent.) were far more than sufficient to neutralise the whole of the acid. When the plant was in full vegetation but had not begun to flower (June 12th), the oxalic acid had increased in proportion to the growth of the plant, but was very unequally distributed, about one half being in the soluble form. The absolute amount was greatest in the leaves, next in the stalk, and somewhat less in the roots and flowers, but the relative proportions do not differ much in different parts of the plant. When the plant was in flower (July 17th), there was a considerable absolute, and a considerable though smaller proportional increase in the amount of oxalic acid, which was still at a maximum in the leaves, and was also abundant in the flowers. The proportion of soluble oxalates becomes greater and greater in passing from the stalks to the leaves, and from the leaves to the flowers. All the parts contain no

deficiency of calcium, but the insoluble oxalates predominate in the stalks. At an advanced stage of fructification (September 14th), both the absolute and relative quantities of oxalic acid had diminished, the absolute quantity being greatest in the flowers, whereas the relative proportion was greatest in the leaves. The relative proportion of insoluble oxalates had generally increased, but in the roots the proportion of soluble oxalates had become somewhat high, a fact which indicates that towards the end of vegetation the root absorbs little or nothing from the soil.

Mesembrianthemum cristallinum.—The seed does not contain oxalic acid. In the early stage of growth (June 9th), a considerable quantity of oxalic acid is formed, a part being in the soluble form. Alkaline salts are abundant and the juice is neutral. As growth proceeds (July 8th), the juice becomes acid and the soluble oxalates predominate, the greatest proportion being found in the leaves. At a later stage, when flowers begin to open (September 25th) the juice is neutral in the root, but is acid in the stalks and especially in the leaves. C. H. B.

Pollen of Coryllus Avellana and Pinus Sylvestris. By E. Schulze and A. v. Planta (*Zeit. physiol. Chem.* **10**, 326—330).—The pollen grains of *Corylus* contain 4·8 per cent. of nitrogen and 14·7 per cent. of cane-sugar; those of *Pinus* contain 2·6 per cent. of nitrogen and 11·24 per cent. of cane-sugar. From 1300 grams of the pollen of the former plant 1 gram of vernine was obtained; vernine was also present in the pollen of the pine but in smaller quantities. Minute quantities of guanine, and probably also of hypoxanthine and adenine, were present in the pollen of both plants; asparagine was absent. W. D. H.

Organic Carbon in Soils which Absorb Free Nitrogen. By Berthelot (*Compt. rend.*, **102**, 951—954).—In order to estimate the organic carbon insoluble in water and hydrochloric acid, a quantity of the soil dried at 100° was treated with excess of hydrochloric acid, and the evolved carbonic anhydride was dried by means of sulphuric acid, absorbed in potash, and weighed. The insoluble residue was washed with water, dried and burnt by means of cupric oxide and oxygen. To estimate the total organic carbon, a second quantity of the dried soil was treated with a slight excess of hydrochloric acid above that required to decompose the carbonates, dried, and burnt with suitable precautions. The following results, expressed in grams per kilo., were obtained (see table, p. 737).

1 kilo. of the different soils which absorb free nitrogen contains 1—2 grams of organic matter which constitutes the agent by which the fixation is brought about. The ratio between the soluble and insoluble carbon varies according to unknown conditions. The ratios between the amounts of carbon and nitrogen seem to indicate that the insoluble organic matter (or organic matter rendered insoluble by the action of heat and acids) consists mainly of albuminoïds, whilst the soluble organic matter consists mainly of carbohydrates.

	Organic carbon.			Organic nitrogen.	Combined carbonic acid.
	Total.	Soluble.	Insoluble.		
Argillaceous sand No. 1	0·819	0·638	0·181	0·093	0·020
Argillaceous sand No. 1, treated differently	1·908	0·704	1·204	0·094	0·081
Argillaceous sand No. 2	1·784	1·244	0·540	0·141	0·878
Argillaceous sand No. 2, treated differently	1·908	0·852	0·328	0·139	0·328
Kaolin No. 1	0·916	0·233	0·683	0·025	0·133
„ treated differently	1·171	0·214	0·957	0·024	0·219
Kaolin No. 2	0·563	0·361	0·202	0·067	0·068
„ treated differently	1·209	0·630	0·579	0·065	0·101

C. H. B.

Nitrogen Compounds in Rain Water. By BERTHELOT and ANDRÉ (*Compt. rend.*, **102**, 957).—Rain water not only contains nitrogen in the form of ammonia and nitrates and nitrites, but also in the form of soluble organic compounds which are not decomposed by boiling with alkalis, and insoluble nitrogenous particles derived from the air. It is essential to estimate all four quantities. Moreover, the analysis should be made immediately after the fall of the rain, and the latter should not be allowed to stand in the collecting apparatus for any considerable time, since that would give opportunity for the development of organisms derived from the air.

C. H. B.

Comparison of Ensilage with Hay as Fodder. By L. BROEKEMA and A. MAYER (*Landw. Versuchs-Stat.*, 1886, 407—417).—The milch cows were fed for definite periods with hay and with sour ensilage which was prepared from the same grass as the hay. These foods appeared to produce equal quantities of milk, but the ensilage raised the yield of fat 0·3 per cent., although it had no influence on the other constituents of the milk. An important observation was made during the experiments, namely, that the cows lost weight during the period in which they were fed with ensilage; the figures actually observed do not in all probability represent the absolute loss of flesh, for seeing that the ensilage is a watery food, a considerable excess of water would be retained in the tissues, and this excess would mask in part the loss of flesh; the minimum loss in weight was probably 80 kilos. per beast. The authors refer to some experiments by Bauduin, which corroborate their own; in these three cows fed on ensilage with accompanying dry fodders whilst losing 40 kilos. in weight, gave 75 litres more milk than three other cows fed on hay, &c. On the other hand, heifers in milk made more use of hay than of ensilage.

E. W. P.

Employment of Sulphate of Copper with Lime as a Preventative of Mildew. By E. PRILLIEUX (*Bied. Centr.*, 1886, 333—335).—The author was deputed by the French Government to inquire

into reports of the good effect of a mixture of sulphate of copper and quicklime as a preventative of mildew, *Peronospora viticola*, on the vine.

He found that it had long been the custom in certain districts of Médoc, in vineyards through which public roads passed, to thickly sprinkle the five or six rows of vines bordering the road with this mixture, to prevent the inroads of children, &c., when the mildew appeared, the vines which had been so treated escaped the disease; and this becoming known to the farmers, they used it generally with excellent results.

The proportions used were 25 kilos. of sulphate dissolved in 225 litres of water, to which was then added 25 kilos. of quicklime as milk of lime—the somewhat thickish mass of a greyish-blue colour was sprinkled with a broom over the vine stems. When thus treated those already attacked were cured; even in cases where the foliage had fallen, it grew again, and the vines produced good fruit which ripened. Equally good results followed its use in other districts.

J. F.

Copper in Vines treated with Copper Sulphate and Lime. By A. Millardet and U. Gayon (*Bied. Centr.*, 1886, 336—338).—The authors found that wines made from grapes grown on vines treated with lime and copper sulphate, were free from copper, whilst the leaves, stalks, and skins contained much of the metal—the leaves contained the most. J. F.

Analytical Chemistry.

Colorimetric Determinations. By G. Giannetti (*Gazzetta*, **16**, 65—73).—In this paper a description of an apparatus is given, devised for the simplification and acceleration of colorimetric determinations. The principle consists in projecting the images of the standard tinted liquid and the solution to be compared side by side on a mirror, the whole being inclosed within a rectangular box, provided with folding doors. An arrangement is also added for syphoning off a portion of the solution to be estimated, and adding water to dilute the tint to the required degree. V. H. V.

Estimation of Chloride of Lime, &c., by Means of Hydrogen Peroxide. By G. Lunge (*Ber.*, **19**, 868—871).—5 c.c. of a turbid solution of chloride of lime (10 grams in 250 c.c. of water) are put into the decomposing flask of a nitrometer (compare Abstr., 1885, 1267). An excess of hydrogen peroxide (about 2 c.c. of the commercial product) is put into the inner tube; the flask is then fitted on to the india-rubber stopper, and the tap turned so that the flask communicates with the measuring tube, the mercury being at zero. The flask is inclined so that the liquids mix; in 1—2 minutes the

reaction is complete, and the oxygen is measured according to Winkler's method (*Ber.*, **18**, 2533). The volume of oxygen corresponds with that of the active chlorine in the bleaching powder.

This method has the advantage of being independent of any normal solution, and also of being quicker than any other. It gives as sharp results as Penot's method. N. H. M.

Klobukoff's Method for the Estimation of Sulphur. By C. Friedheim (*Ber.*, **19**, 1120—1127).—The author has carefully tested this method (Abstr., 1885, 1159). In all cases, his results have been much too low, separated sulphur and traces of sulphuric acid always remaining in the decomposing flask. The author thinks it may be possible to obtain accurate results by this method if the conditions (of dilution, &c.) are observed which must be specially determined for every substance, but that the method is not generally applicable. L. T. T.

Estimation of Sulphuric Acid and Ethereal Hydrogen Sulphates in Urine. By E. Salkowski (*Zeit. physiol. Chem.*, **10**, 346—360).—For the estimation of these substances in urine, the following modification of Baumann's method (*ibid.*, **1**, 71) is recommended:—

For the estimation of the total sulphuric acid, 10 c.c. of hydrochloric acid is added to 100 c.c. of urine, and the mixture heated for a quarter of an hour; barium chloride is then added in excess, and the mixture warmed until the precipitation is complete, when it may be filtered either immediately, or, for complete accuracy, after waiting 24 hours; in the latter case, it is not necessary to warm the mixture after adding the barium chloride.

For the estimation of the ethereal hydrogen sulphates, 10 c.c. of hydrochloric acid seems to be sufficient, in spite of the somewhat greater volume of the liquid; one may, however, add more without any harm. After an hour's warming on the water-bath (temperature 100°), it may be heated over the flame; filtration can be performed forthwith, or if the quantity of barium sulphate is small, it is better to wait 24 hours. W. D. H.

Estimation of Ammonia in Soils. By Berthelot and André (*Compt. rend.*, **102**, 954—956).—When soils are dried at 100° previous to the estimation of the ammonia, there is always a loss of ammonia, which varies with the time of drying and the nature of the soil, but which frequently amounts to 50 or even 75 per cent. of the total quantity present. Even when the drying takes place in a vacuum at the ordinary temperature, there is a distinct, although much smaller, loss, which is greatest with vegetable soils, and practically *nil* with kaolin.

Soils, when moistened, tend continually to lose ammonia during the process of drying spontaneously in contact with the air. This loss is greatest with soils which contain earthy carbonates, owing to the formation of ammonium carbonate which is partly decomposed in contact with water, and it is least with clay. C. H. B.

Remarks on Berthelot and André's Paper on the Estimation of Ammonia in Soils. By T. Schloesing (*Compt. rend.*, **102**, 1001—1003).—The author has never applied his method of estimating ammonia to vegetable soils, and he has never recommended the use of a concentrated solution of soda. His former experiments show that soil, whether dry or moist, absorbs ammonia from the air until the tension of the ammonia in the soil is equal to that of the ammonia in the air. If the soil is moist, the ammonia is converted into nitrates in proportion as it is absorbed, and its tension in the soil is therefore always lower than its tension in the air. The author points out that the soils with which Berthelot and André observed a loss of ammonia when dried in a vacuum at the ordinary temperature, were exceptionally rich in nitrogenous organic matter. C. H. B.

Estimation of Ammonia in Soils: a Reply to Schloesing. By Berthelot and André (*Compt. rend.*, **102**, 1089—1091).

Detection of Nitric in Presence of Nitrous Acid. By A. Piccini (*Gazzetta*, **16**, 108—110).—Warington (Abstr., 1885, 593) in a critical examination of the methods for the detection of nitrous and nitric acids in presence of each other, has pointed out that the process proposed by the author, which consists in the destruction of the former by boiling acidified solution with carbamide, is unsatisfactory, inasmuch as it is impossible to acidify solutions of nitrites in presence of air without the production of nitrates. In answer, it is here allowed that such a change would occur, if the acid were added indiscriminately to the solution to be examined, but if the carbamide is added first, and then a solution of carbamide acidified with sulphuric acid be cautiously delivered at the lower part of the solution by means of a finely drawn out tube, the nitrous acid is completely destroyed before any of it comes in contact with the air. As regards the method for the quantitative determination of nitrites in presence of nitrates, which consists in boiling the solution with a neutral ferrous salt (Abstr., 1881, 1081, and this vol., p. 418), the author thinks also that Warington has somewhat misapprehended his method for the separation and determination of nitric and nitrous acids. The author has shown that the nitric acid may be determined as nitric oxide after all the nitrite has been decomposed, using ferrous chloride.

V. H. V.

Estimation of Phosphoric Acid in Basic Slag. By J. Klein (*Chem. Zeit.*, **10**, 341).—Kosmann's method (this vol., p. 489) does not always give concordant results, and Brunneman's method is open to objections. The author, therefore, recommends fusing the slag with a mixture of 4 parts by weight of the mixed carbonates of sodium and potassium, and 1 part by weight of potassium chlorate. The fused mass being examined in the usual manner. D. A. L.

Some Causes of Discrepancy in Analyses of Superphosphate. By S. Metger and A. Emmerling (*Chem. Zeit.*, **10**, 527—528).—The manner of preparing the solution from a sample of super-

phosphate influences to some extent the amount of soluble phosphate found. For example, when the preliminary mixing with water is made by rubbing vigorously in a mortar, higher results are obtained than by mixing gently. In like manner, shaking frequently and briskly during a short period of digestion with the full quantity of water yields higher results than prolonged digestion with shaking at longer intervals. A combination of vigorous mixing with frequent shaking gives only a slightly greater increase than when the first operation is used alone. With regard to the influence of temperature, solutions prepared at 5—7° yield results slightly lower than those obtained from solutions made at temperatures varying from 18 to 30°. It is evident that some sort of uniformity ought to be observed in the preparation of solutions of superphosphate for analysis. Dissolved bone-meal is not influenced in this manner. D. A. L.

New Method for Estimating Soluble Phosphates. By A. EMMERLING (*Landw. Versuchs-Stat.*, 1886, 429—439).—The solutions required are sodium hydroxide 1 c.c. = 0·005 P_2O_5 ($4NaOH : P_2O_5$); calcium chloride prepared by dissolving 200 grams of the dried salt in 1 litre of water, and then carefully neutralising; phenolphthaleïn, 1 : 500; methyl-orange, a sufficiency dissolved in water to produce a deep orange-yellow. The process employed is the following:—200 c.c. of a solution of superphosphate is mixed with 50 c.c. of the calcium chloride solution. One burette is filled with this mixture, whilst another is filled with the normal soda; then 20, 10, or 5 c.c. of this last are poured into a beaker glass, according to the strength of the superphosphate, the richer samples requiring more soda, distilled water and 2 c.c. of phenolphthaleïn are added, and finally the superphosphate calcium chloride is allowed to flow in rapidly, until the colour of the indicator is somewhat paled; then it is added slowly two drops at a time, until all redness has disappeared. The exact end is difficult at first to determine, for owing to the large amount of indicator added, the final change is not sharp. It is advisable, therefore, to add soda until all redness has gone, and the colour is pale brown or yellow. The determination should be made twice at least, when the exact number of c.c. will be known; the quantity of superphosphate solution, which is shown by the above titration to be necessary to neutralise the soda, is measured out, diluted, and mixed with 4—6 drops of methyl-orange solution; this is then titrated with soda, when the percentage of free acid is estimated. The calculation is as follows:—Weight of superphosphate = 20 grams dissolved in 1000 c.c. H_2O, clear filtrate employed = 200 c.c., and brought up by addition of 50 c.c. $CaCl_2$ to 250 c.c., the measured quantity of soda solution, a c.c. by titration with superphosphate calcium solution required b c.c.; for neutralisation of the free acid in b there was required of soda solution c c.c. Strength of normal soda solution expressed as $P_2O_5 = t$ c.c.

Then we have percentage of soluble phosphate—

$$= (a-c) \times t \times \frac{250 \times 1000 \times 100}{200 \times b \times 20}.$$

It is, however, simpler to reduce $\frac{t \times 250}{200}$ to a constant: in an example given $t = 0{\cdot}004981$ P_2O_5, when $\frac{t \times 250}{200} = 0{\cdot}006277$.

The presence of iron does not affect the results, which compare favourably with those obtained by the uranium or molybdenum methods, a maximum difference of 0·25—0·29 having been observed. E. W. P.

Reich's Method of Determining Arsenic. By L. W. McCay (*Amer. Chem. J.*, **8**, 77—89).—It is shown that, from a nitric acid solution, every trace of an arsenate may be thrown down as silver arsenate without any free silver oxide, by making the liquid neutral or very faintly alkaline with ammonia. The precipitate may be determined by Reich's original method (determination of the contained silver by cupellation); by a modification of Pearce's method (*Chem. News.*, **48**, 85); by the author's former modification (Abstr., 1883, 1034); or by the present method, in which the washed precipitate is dissolved off the paper by a little ammonia, the solution evaporated to dryness and the residue weighed. If chlorides are also present, the silver arsenate is dissolved off the paper in nitric acid, the greater portion of the acid removed by evaporation, the residue treated with a little ammonia, and then very gently ignited before being weighed. The presence of antimony does not interfere; phosphorus, molybdenum, &c., must, however, be removed. H. B.

Estimation of Boric Acid. By H. Gilbert (*Dingl. polyt. J.*, **259**, 383).—Stolba's process for estimating the water in boric acid by ignition with 4 parts of borax, is not applicable when sulphuric acid is present. The author adopts the following method:—1·5 grams of calcium hydroxide are ignited in a platinum dish until the weight is constant. The residue is moistened with 10 c.c. of water and mixed with 2 grams of boric acid. The mixture is evaporated to dryness on the water-bath, heated cautiously to redness and weighed. The loss in weight gives the water. In testing boric acid from Tuscany, the loss represents water and ammonia. It is, therefore, necessary to determine the latter separately and deduct the weight from the total loss obtained. Samples of boric acid from Tuscany (I) and California (II) had the following composition:—

	H_2O.	NH_3.	Na_2O, K_2O.	CaO.	MgO.
I.....	42·03	1·23	0·72	0·40	0·83
II.....	45·29	—	1·01	0·47	0·15

	Fe_2O_3, Al_2O_3.	Cl.	SO_3.	B_2O_3.	Insoluble.
I.....	0·28	0·06	7·04	46·47	0·96
II.....	0·07	0·97	1·17	50·87	0·22

D. B.

Examination of Lead Dioxide. By P. Ebell (*Dingl. polyt. J.*, **260**, 191).—On distilling 0·5 gram of lead dioxide with hydrochloric acid, collecting the chlorine in a solution of potassium iodide, and

titrating with sodium thiosulphate, the author found 95·8 per cent. of PbO_2. To avoid the distillation which is said to be troublesome, it is proposed to treat 0·5 gram of lead dioxide with water, and gently heat the mixture with an excess of concentrated hydrochloric acid. The lead tetrachloride thus formed is then mixed with potassium iodide, and the iodine titrated with sodium thiosulphate; 95·6 per cent. of PbO_2 was obtained. When powdered lead dioxide is added to an acid solution of hydrogen peroxide (the latter being in excess), the following reaction takes place: $H_2O_2 + PbO_2 + 2HNO_3 = Pb(NO_3)_2 + 2H_2O + O_2$; the unattacked hydrogen peroxide is then titrated with potassium permanganate. Obtained 96·08 per cent. of PbO_2. By utilising this reaction, lead dioxide may be determined gasometrically, the oxygen evolved being measured in Lunge's nitrometer. The results, however, appear somewhat low. D. B.

Detection of Metallic Mercury and Mercuric Chloride in the Toxicological Examination of Organic Substances. By M. T. Lecco (*Ber.*, **19**, 1175—1176).—When metallic mercury is precipitated from solution by means of stannous chloride, it forms a grey powder very difficult to collect and wash; if, however, the precipitation be performed in an evaporating dish, the supernatant liquid poured off as completely as possible, and the residue dried on the water-bath, the metal forms globules which may be readily washed and collected.

Mercuric chloride when mixed with organic matter, food, &c., is slowly reduced to the metallic state, this reduction is usually quite complete in about six weeks at the ordinary temperature, but if the mixture be boiled it takes place immediately; the presence of corrosive sublimate can accordingly only be detected by dissolving out with cold alcohol or ether before heating.

On distilling foods, &c., containing metallic mercury precipitated in the above manner and therefore in a very fine state of division, a small quantity of the mercury passes over with the steam.

A. P.

Colorimetric Estimation of Sulphur in Iron. By J. Wiborgh (*Dingl. polyt. J.*, **260**, 179—182).—The sample of iron is dissolved in dilute sulphuric acid, and the gas evolved is allowed to pass through a piece of cloth saturated with a metallic salt (best cadmium nitrate). The sulphide formed by the action of sulphuretted hydrogen imparts a certain colour to the cloth, and from its intensity the percentage of sulphur is estimated. D. B.

Estimation of Fusel Oil. By J. Traube (*Ber.*, **19**, 892—895).—The author has already shown (Abstr., 1885, 866 and 1033) that the height in a capillary tube of aqueous solutions of organic substances of one series often decreases considerably with increasing molecular weight of the substance dissolved. A very small amount of fusel oil present in diluted brandy influences the height of the brandy in a capillary tube. Propyl and butyl alcohols and the various aldehydes present in the fusel oil lower the height more than ethyl and less than amyl alcohol. The apparatus used is that previously

described (*loc. cit.*). The sp. gr. of the brandy is first determined, and the brandy then diluted so as to be nearly 20 per cent. The height in a capillary as compared with pure 20 per cent. spirit shows at once the amount of fusel oil present, even when in smaller quantities than 0·1 per cent. N. H. M.

Determination of Phenol in Crude Carbolic Acid. By J. Tóth (*Zeit. anal. Chem.*, **25**, 160—164).—This is a modification of Koppeschaar's method, which depends on the conversion of the phenol into tribromophenol by a known excess of bromine, and the titration of the unabsorbed bromine. The crude carbolic acid is shaken with its own volume of potash (1·3 sp. gr.) for half an hour, then diluted, filtered from tarry matters, which are well washed with warm water, and, after making feebly acid with hydrochloric acid, is further diluted until it contains not more than 0·4 per cent. of phenol. 50 c.c. is then mixed with 150 c.c. of a solution containing 2·04 grams of sodium bromate and 6·959 of bromide per litre; 5 c.c. of strong hydrochloric acid is added, and then, after 20 minutes, excess of potassium iodide. The liberated iodine is titrated with thiosulphate as usual. M. J. S.

Phenylhydrazine as a Test for Sugar in Urine. By R. v. Jaksch (*Zeits. Klin. Med.*, **11**, 20—25).—The compound of phenylhydrazine and sugar that Fischer (*Ber.*, **17**, 579) has described furnishes a delicate test for dextrose in clinical work. When a solution of phenylhydrazine hydrochloride, containing also sodium acetate, is added to a solution of sugar, a yellow precipitate of needles of phenylglucazone, occurring both singly and in bundles, forms in a few minutes. The formation of crystals takes longer in a dilute solution of dextrose: the sediment should be examined microscopically, and for certainty its melting point (204—205°) ascertained. By this test sugar is never found in normal urine; it can be detected in the urine of diabetic patients when it is present in too small a quantity to give the ordinary tests; it possesses an advantage over the copper test in that other reducing substances occur in urine besides sugar. In the urine of persons poisoned by arsenic, sulphuric acid, or by potash, there are reducing substances present, but by this test no sugar: but in that of persons poisoned by carbonic oxide or by other irrespirable gases, the occurrence of sugar seems constant. When the urine is strongly albuminous, the proteïd must be first separated by heat. A small quantity of albumin, however, does not interfere with the test. In blood and dropsical fluids, sugar can always be detected by this test: it is necessary to precipitate and filter off the proteïds before applying the test. W. D. H.

Clinical Examination of Urine by Means of Fehling's Solution. By L. Jolly (*J. Pharm.* [5], **13**, 388—390).—This reagent affords information as to the presence of (1) peptones; (2) uric acid in excess; (3) phosphoric acid in excess; (a) in presence of little uric acid; (b) in a urine rich in uric acid; and (4) glucose. (1.) 1 c.c. of Fehling's solution is mixed with 8—10 c.c. of urine; the

mixture is turbid and blue. This turbidity may be due to lime, calcium phosphate, and copper phosphate. Heat to incipient boiling. A. *The solution remains blue.* No particular indication. B. *The solution is decolorised* with formation of an amber-coloured flocculent precipitate suspended in the liquid = peptone. C. *The liquid takes an orange tint.* After standing a few moments the precipitate settles and has an orange colour = glucose. (2.) Equal parts of Fehling's solution and urine are mixed and heated to boiling. A. *There is little change of colour.* Allow to remain some minutes. B. The cleared liquid remains blue; the urine contains only little uric acid. The precipitate is bluish-grey. C. The cleared liquid is green; the urine contains an excess of uric acid or urates. The precipitate is greenish-grey. When the precipitate is small in amount, the urine is poor in phosphoric acid. When the precipitate is very abundant, the urine is very rich in phosphoric acid. D. The liquid takes an orange tint. On remaining, the clear liquid has a brown tint. If the precipitate has a deep colour tending towards red, it indicates glucose. Observe that with equal quantities of urine and Fehling's solution the peptones are not manifested. Accordingly, however small the amount of copper reduced, it should always be attributed to glucose. A urine containing not more than 3 to 4 grams of sugar per litre gives a very sensible reaction under these conditions. (3.) 1 c.c. of urine and 4—5 c.c. of Fehling's solution are mixed and heated to boiling. A. If there is no colour-change, no indication. B. If the liquid changes colour from dull greenish-yellow to bright orange, it indicates glucose. The different tints depend on the quantity of sugar present, and consequently on the more or less complete reduction of the copper.

J. T.

Value of Brücke's Method for the Removal of Interfering Substances from Urine in Testing for Glucose. By E. M. Green (*Amer. Chem. J.*, **8**, 139—152).—In the precipitation of the urine by lead acetate and tribasic lead acetate there is always a certain loss; this, however, is very variable, not being the same for two estimations conducted side by side. The average loss in the two precipitations may however be valued at 15—16 per cent. on urine containing 1—2 per cent. of glucose, and 31 per cent. on urine containing 0·5 per cent. of glucose.

H. B.

Detection of Grape-sugar in Leather. By B. Kohnstein (*Dingl. polyt. J.*, **259**, 560—563).—In order to increase the weight of leather, syrup is frequently employed as a substitute for grape-sugar. Different samples of syrup found in commerce had the following composition:—

	I.	II.	III.	IV.
Water	14·53	14·20	16·32	19·80
Grape-sugar	20·00	31·80	35·01	31·03
Organic non-saccharine matter	64·68	53·53	48·09	48·81
Ash	0·49	0·47	0·58	0·36

The determination of the grape-sugar with Fehling's solution is

therefore not sufficient, as the remaining constituents of the syrup are ignored. Moreover, leather tanned with pine bark, sumach, or valonia, contains substances which reduce Fehling's solution, whilst leather prepared with extracts of tannin takes up foreign substances, which cannot without difficulty be distinguished from the non-saccharine constituents of potato syrup.

The author employs the following method:—20 to 25 grams of leather cuttings is dried at 100°, and weighed to ascertain the percentage of water present. The dried substance is then extracted four or five times with warm water, the solution filtered, and the filtrate made up to 500 c.c. 100 c.c. of the solution is evaporated to dryness, weighed, and the residue containing tannin, colouring matters, gallic acid, sugar, dextrin, and other extractive substances, is ignited, and the ash weighed. To determine whether foreign substances have been added to leather, 200 c.c. of the original extract is agitated with 6 grams of freshly ignited magnesium oxide, until the clear solution ceases to give a reaction with iron and gelatin. Magnesium oxide precipitates the tannin, the colouring matters and gallic acid, leaving the remaining constituents in solution. The mixture is filtered, and a certain quantity of the filtrate evaporated to dryness, weighed, ignited, and re-weighed. The difference between the two weighings, after deducting the ash, gives the amount of tannin, colouring matters, and gallic acid, contained in the leather, whilst the quantity of the remaining substances extracted by water is calculated from the second weighing. The sugar is determined by treating 50—60 c.c. of the first extract with an excess of Fehling's solution, washing the precipitate, dissolving it in hydrochloric acid, and determining the copper in the solution by precipitation as sulphide. The difference between the weight of original extract obtained and that of tannin, colouring matters, gallic acid, and sugar found, gives the amount of foreign substances added to leather besides sugar. D. B.

Estimation of Undissolved Starch in Sweet Mash. By J. Spitzer (*Dingl. polyt. J.*, **260**, 144).—After triturating 500 c.c. of unfiltered mash in a mortar, 100 c.c. is diluted with 300 c.c. of water, heated at 70° for 20 minutes, and made up to 1 litre. 50 c.c. of the mixture is then transferred to a metal vessel holding 100 c.c. or to a Lintner's "pressure-bottle," heated to boiling for 20 minutes, allowed to cool to 70°, treated with 5 c.c. of malt extract, digested on the water-bath at 70° for 20 minutes, treated with 5 c.c. of a 1 per cent. solution of tartaric acid, and heated for half an hour at a pressure of three atmospheres. After cooling the mass to 70°, it is digested with 5 c.c. of malt extract, transferred to a 250 c.c. flask, and filtered. 200 c.c. of the filtrate is then inverted with hydrochloric acid, the solution diluted to 300 c.c., and the dextrose determined with Fehling's solution. In a second portion of the mash, the total amount of dextrose is determined by diluting, filtering, and inverting, as in the preceding case. The difference between the two dextrose-values gives the quantity of "undissolved" starch. D. B.

Valuation of Calcium Acetate. By H. PHILLIPS (*Chem. News*, **53**, 181—182).—1 gram of the sample is placed in a small retort together with 50 c.c. of water containing 10 c.c. of a 40 per cent. solution of phosphoric acid, and the whole distilled until only 5 c.c. remains behind. 50 c.c. of hot water is now added, and the distillation conducted as before; finally another 50 c.c. of water is added and distilled off. The acetic acid is titrated in the combined distillates. To reduce the inconvenience due to frothing, the neck of the retort is inclined upwards during distillation. D. A. L.

Estimation of Resin (Colophony) in Soaps and Fats. By A. GRITTNER and J. SZILASI (*Chem. Zeit.*, **10**, 325).—About a gram or two of soap is dissolved by warming with 80 per cent. alcohol, and when necessary the solution is neutralised with ammonia; it is then treated with a 10 per cent. alcoholic solution of calcium nitrate, stearic, palmitic, and (part of the) oleic acids are precipitated and removed by filtration. The clear filtrate is treated with excess of silver nitrate and diluted, silver resinate and oleate are precipitated. The precipitate is washed, dried at 70—80°, and extracted with ether, which dissolves the resinate readily but the oleate only sparingly. The ethereal solution is run into a graduated vessel, the silver salt decomposed with hydrochloric acid, an aliquot part of the clear solution evaporated and the residue (the resin) weighed. A deduction of 0·0016 gram per 10 c.c. of ether solution must be allowed for oleic acid. D. A. L.

Action of Nitrous Acid on Urea, Uric Acid, and Ammonium Sulphate. By A. EMMERLING (*Landw. Versuchs-Stat.*, 1886, 440—450).—After examination of the work done in this direction by Liebig, Kreusler, and others, the author concludes that as the results vary so much, the decomposition of urea is dependent not only on the temperature and the strength of the acid, but also on the time. He, therefore, employing the process he has formerly described (*Landw. Versuchs-Stat.*, **24**, 121), examined the actions of acetic acid and potassium nitrite on urea when warm and cold; nitric acid and potassium nitrite both hot and cold; nitrous acid on ammonia sulphate; and nitrous acid on uric acid. In no case, nor under any circumstances, was it possible to obtain all the nitrogen, even when all allowances were made for experimental errors. The results obtained were equally unsatisfactory when the operation took place in a vacuum, although it was observed that a considerable time is required for the completion of the operation. E. W. P.

Error in the Estimation of Urea by the Hypobromite Method with Russell and West's Apparatus. By W. D. GREEN (*Amer. Chem. J.*, **8**, 124—127. Compare this Journal, 1874, 749). A certain amount of carbonic anhydride escapes absorption by the alkaline solution. Using 1—4 c.c. of a 5 per cent. solution of urea, from 0·25 to 2·5 c.c. of carbonic anhydride may be carried with the nitrogen into the measuring apparatus. H. B.

New Method for the Determination of Uric Acid. By J. B. Haycraft (*Zeit. anal. Chem.*, **25**, 165—169).—This method is based on the almost absolute insolubility of silver urate in ammonia. The urine (after removal of albumin, if present) is mixed with hydrogen sodium carbonate, which is found to prevent reduction of silver, then with ammonia and ammonio-nitrate of silver. The gelatinous precipitate is best collected and washed on an asbestos pressure-filter. After thorough washing, it is dissolved in nitric acid and the silver determined by Volhard's thiocyanate method (Abstr., 1878, 743): 1 c.c. of centinormal thiocyanate corresponds to 0·00168 gram of uric acid. Test analyses showed errors of deficiency of only 1 or 2 mgrms. The author ascribes the irregularity in the composition of silver urate found by Salkowski, partly to the simultaneous precipitation of ammonium magnesium phosphate and partly to the fact that Salkowski overlooked the reduction of the silver, the amount of which varies with time and temperature. M. J. S.

Detection of Alkaloïds in Urine by Means of Iodine Solution. By Chibret and Izarn (*Compt. rend.*, **102**, 1172—1173).—The delicacy is increased by concentration of the reagent (iodine, 8 parts; potassium iodide, 10 parts; water, 10 parts), by cooling the solution to 0°; and by employing a brilliant light concentrated by means of a condensing lens, the test-tube being placed against a black background. The green fluorescence is then readily seen, and 0·0005 part of morphine in solution gives a distinct reaction.

The proportion of alkaloïds in urine passed eight hours after waking is five times as great as in the urine of the other hours of the day. This result confirms Bouchard's determination of the maximum toxic action of this urine. C. H. B.

Detection of Albumin. By H. Prunier (*J. Pharm.* [5], **13**, 501—502).—The author refers to Méhu's criticism on Tanret's reagent for albumin (Abstr., 1885, 451), and asserts that Musculus's method is similarly liable to error. The latter process as applied to urine, for example, consists in pouring nitric acid carefully down the side of a test-tube containing the urine, so that the acid forms a layer underneath the urine. In presence of albumin, a whitish turbidity makes its appearance as the two liquids slowly mix. The author has, however, frequently obtained this turbidity in urine which gave no turbidity on boiling, or on heating with saturated sodium sulphate solution and acetic acid, nor with this acid and potassium ferrocyanide; microscopic examination did not show the crystalline forms of uric acid. Further investigation showed the reaction to be due to peptone. The method in question should always be controlled by boiling with sodium sulphate and addition of acetic acid.

J. T.

General and Physical Chemistry.

Absorption-spectra of Oxygen. By J. Janssen (*Compt. rend.*, **102**, 1352—1353).—Oxygen not only gives the spectrum of fine lines described by Egoroff, but also a series of shaded bands very difficult to resolve. This second spectrum appears much later than the first at moderate pressures, but develops rapidly as the density increases, and soon predominates over the line spectrum. Each spectrum can be obtained independently of the other.

When the density of the gas and the thickness of the absorbing layer both vary, the intensity of the absorption-bands does not vary in proportion to the product of the density into the thickness of the layer, but in proportion to the product of the thickness into the square of the density. C. H. B.

Spectra of Erbia. By W. Crookes (*Proc. Roy. Soc.*, **40**, 77—79).—The phosphorescent spectrum of erbia, obtained free from yttria, samaria, and allied oxides, consists of four green bands, λ5564, 5450, 5318, and 5197. The substance itself is of a rose-pink colour; it gives a spectrum of sharp and distinct black lines and bands when illuminated by reflection from the sun or electric arc. The absorption-spectrum of erbic chloride, the incandescent spectrum of the oxide, and the spark spectrum taken from a concentrated acid solution of the chloride, are also mapped out. V. H. V.

Comparative Effect of Different Parts of the Spectrum on Silver Salts. By W. de W. Abney (*Proc. Roy. Soc.*, **40**, 251—252).—In a former paper (Abstr., 1882, 565), it was pointed out that mixtures of the iodide and chloride, or iodide and bromide of silver, give rise to peculiar photographic spectra, in which there are revealed a minimum action at G, and consequently two maxima. Subsequently Schumann has contested this result, stating that if silver bromide and iodide are precipitated simultaneously no such phenomenon occurs, but that a mixture of the salts after separate precipitation does give rise to such a double maximum. In this paper, experiments made with a sensitometer are described; various salts of silver and combinations of them were tried with the same result, and the former and disputed results confirmed. V. H. V.

On Colour Photography in Natural Colours. By H. W. Vogel (*Ann. Phys. Chem.* [1], **28**, 130—135).—The author remarks that the rule that blue and yellow pigments when mixed together give green is not universally true, but that several new aniline yellows and blues, for instance chrysaniline and aniline-blue, produce red when combined. Further, he finds that very few violet pigments owe their colour to light of violet refrangibility, but to blue and red. Methyl-violet

when looked at through ammoniacal copper oxide appears pure blue and not violet, although the presence of violet rays in the transmitted light is readily recognised by the spectroscope. The same result is obtained with the violet light from a Geissler's tube containing nitrogen.

The author then considers the process for photographing in natural colours, in which three negatives are taken under blue, yellow, and red glass respectively, converted into photolithographic or other printing surfaces, inked with colours complementary to the respective absorbing media, and printed one above the other as usual in colour printing. This process was found not to give good results, nor did later processes in which the same substance (eosin) was used for all three colours to render the plates sensitive; the plates were thus not sensitive for the especial rays they were intended to absorb, nor were the inks really complementary to those of the glass plates. The author suggests using at least six negatives, the silver bromide being rendered sensitive in each case by admixture with a colouring matter which should absorb the tint which it is required to reproduce. From these negatives, blocks are prepared from which the picture is printed with the same colouring matters which were used to sensitise the silver bromide. H. K. T.

Seat of the Electromotive Forces in a Voltaic Cell. By W. E. Ayrton and J. Perry (*Phil. Mag.* [5], **21**, 51—62; comp. Lodge, Abstr., 1885, 1027).—The authors maintain that although there cannot be an E.M.F., as defined by Lodge, due to the junction of two dissimilar metals, yet there may be a large difference of potential. In answer to Lodge's argument that a rise in potential must necessitate an expenditure of energy, they contend that it is conceivable that what is gained in potential energy is lost in some other form of energy. They suppose that when electricity passes from copper to zinc it loses in tension energy what it gains in potential energy, and compare this change to the conversion of the energy of a winding engine into tension energy in the rope. The same analogy is applied to a stream of fluid forced through pipes at different levels, and for which—

$$\frac{v^2}{2g} + 2{\cdot}3p + h = \text{const.},$$

the value $2{\cdot}3p$ being called the pressure energy of the fluid as distinguished from the kinetic energy $\frac{v_2}{2g}$ and the potential energy h. In the same way, the authors compare thermo-electric currents to a fluid in a closed circuit of tubes in which different vertical portions are maintained at different temperatures. The Peltier effect will then be a measure, not of the actual contact difference of potential at a junction, but of the difference in rate of change of contact potential for change of temperature.

The following results are given of new determinations of contact potential differences, by means of the apparatus used in the authors' researches:—

Copper at 16° with clean mercury at 16° had a contact difference of 0·308 volt.

Mercury at 16° with mercury at 26° had a contact difference of 0·75 volt.

Mercury at 26° with copper at 16° had a contact difference of − 1·5 volt.

The results with hot mercury are considered to be somewhat high, owing to invisible films of oxide. H. K. T.

Seat of the Electromotive Forces in Voltaic and Thermo-electric Piles. By O. Lodge (*Phil. Mag.* [5], **21**, 263—276).—This paper is a reply to the criticisms of Ayrton and Perry (preceding Abstract). The author maintains, in the first place, that in the fundamental formula for a thermo-electric circuit—

$$E = f(t_2) - f(t_1),$$

all that can be said about $f(t)$ is that it is a potential function characteristic of the two metals, and is not the contact difference of potential as measured electrostatically by the Volta effect. In support of this, he remarks that the Volta effect is some hundred times greater than any concerned in thermo-electricity, that it has no relation to bismuth or antimony or the thermo-electric order of metals, but is related to the oxygen affinities of metals.

The author further maintains that reversible heat localities, whether Peltier or Thomsen, and seats of E.M.F. are identical in metallic circuits, so that the equation—

$$E = \frac{W}{Q},$$

is true not only for the whole circuit, but also for each point in the circuit, and therefore the E.M.F. of a thermo-electric circuit composed of two metals is made up of four portions, one at each junction, and the other two at each temperature slope, so that—

$$E = (\Delta E)_1 + \int_B dE - (\Delta E)_2 - \int_A dE.$$

If this is not allowed, then it becomes necessary to suppose that electricity has a specific heat like an ordinary fluid, and that the Peltier and Thomsen effects are simply due to changes in this specific heat.

H. K. T.

Electromotive Forces developed during the Combination of Zinc and Iodine in Presence of Water. By A. P. Laurie (*Phil. Mag.* [5], **21**, 290—299).—These experiments were conducted with a view to determining the heat of combination of zinc and iodine in the presence of water. Two forms of cells were used, one consisting of wires of zinc and platinum immersed in a solution of iodine in zinc iodide, the other of a zinc rod and a copper wire coated with cuprous iodide immersed in zinc iodide solution. The changes which take place in the cell are, on the one hand, the combination of zinc and iodine and the solution of the zinc iodide formed, producing heat, on the other, the disintegration of the zinc, the decomposition of the iodine

molecule and the removal of free iodine from solution, absorbing heat. By varying the amounts of either zinc iodide or of iodine in the cells, the heats of solution of these substances are determined.

The author adopts Helmholtz's theory of the relation between heats of combination and electromotive force, namely, that when a small current passes through a cell, a certain amount of heat must be supplied or removed in order to keep its temperature constant, apart from the heat developed by the resistance of the cell. This cooling or heating is measured by noting the variations in the electromotive force due to change of temperature. For these experiments, the galvanometer used was that of Professor Tait. A Daniell cell checked against Latimer Clark cells was used as standard of E.M.F. The following results were obtained:—

(1.) The surface condition of the metals has very little influence on the E.M.F.

(2.) No variation in E.M.F. could be observed in a cell whose temperature was raised from 10° to 30°.

(3.) In a zinc-cuprous iodide cell in which the amounts of zinc iodide were made to vary, 0·003 gram of ZnI_2 in 1 gram of water gave 0·771 volt; 3·90 grams of ZnI_2 in 1 gram of water gave 0·415 volt. There was a sudden fall in E.M.F. when the first addition of zinc iodide was made, and also when saturation was reached. Taking $y = \phi(x)$ as the equation to the curve, where y is the heat due to solution only, then $y = 0$ in a saturated solution, since at this point heat due to solution ceases. Integrating between the limits 0 and 0·044, the heat of solution of 0·044 gram of ZnI_2 in 1 gram of water (ZnI_2,400H_2O) is 13000 cal. This number is somewhat higher than Naumann's.

(4.) In a cell containing 0·33 gram of ZnI_2 in 1 gram of water with varying amounts of iodine, 0·0006 gram of iodine gave 1·221 volt; 0·309 gram of iodine gave 1·287 volt.

(5.) In a cell containing 0·014 gram of iodine in 1 c.c. with varying amounts of zinc iodide, 0·118 gram of ZnI_2 in 1 gram of water gave 1·303 volt; 3·870 grams of ZnI_2 gave 1·075 volt. H. K. T.

Electromotive Force of certain Tin Cells. By E. F. Herroun (*Phil. Mag.* [5], **21**, 13—20).—In this paper the author examines the electromotive force of cells in which tin in solutions of its salts is opposed to different metals in solutions of their corresponding salts. The liquids were separated by a porous cell and were compared with a standard Daniell cell composed of zinc and copper sulphates of a strength 1·8M″SO_4 + 100H_2O.

The E.M.F. was determined by Latimer Clark's zero method, measurements being taken when the cell was first put up and also after it had worked for a short time. The results so obtained were controlled by measuring the current from two or three cells by inserting known resistances. It was found necessary to work with tin solutions containing small quantities of free acid, owing to their tendency to deposit basic compounds. The tin and copper used were obtained by electrolysis; the zinc was the pure metal of commerce and was amalgamated. The following results were obtained:—

Zinc in $0{\cdot}5ZnSO_4 + 100H_2O$, opposed to tin in $0{\cdot}5SnSO_4 + 100H_2O$, both solutions containing 1·5 per cent. H_2SO_4, gave 0·519—0·535 volt, average 0·525 volt.

Tin in $0{\cdot}5SnSO_4 + 100H_2O$, opposed to copper in $0{\cdot}5CuSO_4 + 100H_2O$, solutions containing 1·2 per cent. H_2SO_4, gave 0·56—0·572 volt, average 0·56 volt.

Cadmium in $0{\cdot}5CdSO_4 + 100H_2O$, opposed to tin in $0{\cdot}5SnSO_4 + 100H_2O$, solutions containing 1·5 per cent. H_2SO_4, gave 0·189 volt.

Zinc in $0{\cdot}5ZnCl_2 + 100H_2O$, opposed to tin in $0{\cdot}5SnCl_2 + 100H_2O$, solutions containing 1 per cent. HCl, gave 0·544 to 0·553 volt, average 0·549 volt. The E.M.F. calculated from the heats of formation is 0·684 volt, giving a difference, or "thermovoltaic constant" of 0·135 volt.

Cadmium in $0{\cdot}5CdCl_2 + 100H_2O$, opposed to tin in $0{\cdot}5SnCl_2 + 100H_2O$, solutions containing 1 per cent. HCl, gave 0·247 to 0·262 volt, average = 0·249 volt. Theoretical E.M.F. = 0·326 volt. Difference = 0·077 volt.

It is found generally that where tin is the attacked metal, the presence of free acid in its solution has the effect of raising the electromotive force, whilst the reverse is the case where it is the positive element. This fact is taken into consideration in taking the averages.

Zinc in $0{\cdot}25ZnI_2 + 100H_2O$, opposed to tin in $0{\cdot}25SnI_2 + 100H_2O$ solutions containing 1·5 HI, gave E.M.F. 0·47—0·49, average 0·485 volt. H. K. T.

Electrical Conductivity of Saline Solutions of Mean Concentration. By E. Bouty (*Compt. rend.*, **102**, 1372—1375).—Between 0° and 20°, the resistance of a dilute saline solution is accurately represented by the formula

$$r_t = r_0 \frac{1}{1 + \alpha t^r}$$

and the value of α for moderately dilute solutions differs but little from the value for very dilute solutions, namely, 0·0333 (Abstr., 1884, 882). The ratio between the molecular resistance of a solution of a given salt and that of a solution of potassium chloride of the same molecular concentration is usually greater than 1, but approaches more nearly to 1 the more dilute the solution (*loc. cit.*). If the phenomenon is represented by the expression $R = 1 + f(m)$, in which m is the number of equivalents of the salt in a litre of solution, it is found that if m varies in one geometric progression, $f(m)$ varies in another geometric progression, so that $f(m) = Am^c$. The value of A varies greatly for different salts, but the value of c remains practically constant and equal to $\frac{1}{3}$. The calculated and observed values for solutions of zinc sulphate and lead nitrate agree closely. For dilute solutions the law of equivalents is rigorously exact, but for the same salts with values of m greater that 0·5, $R_0 = 1 + Am^{\frac{1}{3}}$. The value of A for zinc sulphate is 2·959, for lead nitrate 1·116, for potassium sulphate 0·359, and for potassium nitrate 0·240. The mean distance l between the molecules of a salt

is in the inverse ratio of the cube root of the number of molecules in unit space, and hence the last formula may be written $R_0 = 1 + \frac{A}{l}$, or the divergence of a salt in solution from the law of equivalents varies inversely as the mean distance between its molecules. Substituting the value for the molecular resistance, it follows that the excess of the specific resistance of a salt above the limiting value is practically inversely as the mean distance between the molecules, as Kohlrausch has previously stated. C. H. B.

Correlation of Electrolytic Conduction and Molecular Composition. By H. E. Armstrong (*Proc. Roy. Soc.*, **40**, 268—291). —The author elsewhere (*British Association Report*, 1885) has particularly called attention to the affinity of negative elements for one another, and attributed to this property the formation of so-called molecular compounds. In the present paper the attempt is made to show that electrolytic conduction is correlated with molecular composition, and in this connection the doctrine of valency and the nature of chemical change is discussed with particular reference to the "residual affinity" or tendency of combination of the negative elements.

Substances, as regards the action on them of an electromotive force, are generally divided into the three classes:—metals, electrolytes, and dielectrics. Such a classification does not make manifest the difference between substances *per se* electrolytes and those which individually behave as dielectrics but when conjointed act as electrolytes, such as hydrogen chloride and water. The latter class it is proposed to designate by the term *pseudo-dielectrics*, and conducting mixtures of two members of it, *composite electrolytes*, as distinguished from simple electrolytes (AgCl, &c.). As regards the last named, it is to be noted that they are restricted to *metallic* chlorides and salts, including among them the hydroxides and proto-salts, but excluding the acids and per-salts. Hence it can be concluded that the capacity for electrolysis is conditioned not only by the nature of the elements contained in, but also by the molecular structure of a compound.

On the other hand, in the case of the composite electrolytes, there is no satisfactory evidence to show that the constituents of the electrolytes are set free prior to the action of the electromotive force, or are set free by the effect produced by the electromotive force on either member separately; the author holds that an additional influence comes into play, that of the negative radicle of one member of the composite electrolyte on the negative radicle of the other. Thus that in the case of a solution of hydrogen chloride in water, the influence of the strain of the oxygen-atom of the one on the chlorine-atom of the other, superadded to that of the electromotive force, brings about disruption, and consequently conduction. The recent experiments on the electric conductivity of aqueous solutions, especially those by Ostwald (Abstr., 1885, 3, 323, and 1029), favour the above view as demonstrating that the molecular conductivity $m=kv$ increases with dilution, that is to say, the dissolved substance exercises a greater specific effect, finally attaining a maximum, from which it diminishes. Thus the in-

vestigations of Ostwald show that the molecular conductivity of solutions of hydrogen chloride, bromide and iodide is practically the same, whilst that of hydrogen fluoride differs most markedly from them in possessing an exceedingly low conductivity, which but slowly attains a maximum. Now this result is in perfect accordance with our knowledge of these compounds in the gaseous state, the molecule of the former being represented by the expression HCl, &c., whereas that of hydrogen fluoride at a temperature immediately above its boiling point is represented by the formula H_2F_2, and in the liquid state its molecule is probably even more complex. Thus were the three first-mentioned hydrides present chiefly as simply molecules, they should exert their full effect *ab initio;* but in the case of hydrogen fluoride, if the residual affinity be more or less exhausted by the formation of complex molecular aggregates, the initial conductivity will be low and will increase on dilution only as these aggregates are broken up.

Precisely similar are Ostwald's results for nitric, chloric and perchloric acids as compared with iodic and periodic acids the complex nature of which is exemplified by the formation of complex metallic salts. So also the researches of Kohlrausch and Nippoldt show that the resistance diminishes to a much greater extent for equal increments of temperature in concentrated than in dilute solutions of sulphuric acid: a result in accordance with the views enunciated above, as concentrated solutions would be richer in complex aggregates than dilute solutions.

In connection with the theory of valency, the author remarks that no known compound is saturated, for in that case it would be incapable of entering into any interaction; its decomposition would be a necessary prelude to its activity. The most inert and apparently the most nearly saturated compounds are the paraffins, and next to them, hydrogen. Water, popularly regarded as a saturated compound, both in its chemical and physical properties, behaves as eminently unsaturated.

The influence exerted by one set of molecules on another as due to the existence of residual affinity can also be applied to explain the occurrence of chemical change. The researches of H. B. Dixon (Abstr., 1845, 479, and Trans., 1886, 94) have demonstrated that a dry mixture of carbonic oxide and oxygen does not explode, and that their combination is effected *only* along the path of the discharge. These results refute the commonly received opinion that the molecules in the path of the discharge are dissociated, and that the heat developed in the recombination of dissimilar atoms causes the dissociation of other molecules, and this change proceeds *ad infinitum*. So also it was shown that *only* those compounds which would produce water in the course of the change are active in effecting the explosion of carbonic oxide and oxygen. These results would show that for interaction it is not only necessary that the catalyst should be divisible between the interacting substances, but that it should consist of a positive and a negative, not of two negative radicles.

If then a distinction can be drawn between simple and composite electrolytes, the presence of the latter class may be found to be essential to many interactions such as the rusting of iron, the

action of water or acids on metals, conversion of nitric oxide into peroxide. Experiments on these points are for the most part completely wanting. V. H. V.

Heats of Combustion and Formation of Solid Hydrocarbons. By BERTHELOT and VIEILLE (*Compt. rend.*, **102**, 1211—1217).—The substances were burnt in a calorimetric bomb by means of a large excess of oxygen compressed to 24 atmos. The substance was ignited by means of an iron wire heated to redness by an electric current, and a correction was made for the heat of combustion of the wire, and also for the small quantity of nitric acid formed in consequence of the presence of air in the bomb. The following values were obtained :—

	Heat of combustion.		
	At constant volume.	At constant pressure.	Heat of formation.*
Naphthalene, $C_{10}H_8$	+ 1243·9	+ 1245·0	− 29·0
Anthracene, $C_{14}H_{10}$	+ 1706·2	+ 1707·6	− 46·6
Phenanthrene, $C_{14}H_{10}$ ..	+ 1699·0	+ 1700·4	− 39·4
Retene, $C_{18}H_{18}$	+ 2323·6	+ 2326·1	− 13·1
Diphenyl, $C_{12}H_{10}$	+ 1508·7	+ 1510·1	− 37·1
Acenaphthene, $C_{12}H_{10}$ ..	+ 1519·8	+ 1521·2	− 48·1
Stilbene, $C_{14}H_{12}$	+ 1775·6	+ 1777·3	− 47·3
Dibenzyl, $C_{14}H_{14}$	+ 1828·3	+ 1830·2	− 31·2
Phenol, $C_6H_5{\cdot}OH$.....	+ 736·5	+ 737·1	+ 33·9
Camphene, $C_{10}H_{16}$ (inactive, crystallised).	+ 1466·9	+ 1469·2	+ 22·8

From these values the thermal disturbances which accompany the following synthetical reactions can be calculated :—

$$C_6H_6 \text{ gas} + 2C_2H_2 = C_{10}H_8 \text{ solid} + H_2 \text{ develops} + 105{\cdot}2.$$

The heat developed by the condensation of the last 2 mols. of acetylene (55 × 2 cal.) is practically the same as that developed in the formation of benzene (57 × 3 cal.) :—

$$2C_6H_6 \text{ gas} + C_2H_2 = C_{14}H_{10} \text{ solid} + H_2 \text{ develops} + 38{\cdot}5.$$
$$2C_6H_6 \text{ „ } = C_{12}H_{10} \text{ cryst.} + H_2 \text{ absorbs} - 13{\cdot}1.$$

The formation of diphenyl, like the formation of dimethyl (ethane) from methane, results in an absorption of heat. The heats of combustion of anthracene and phenanthrene, and of diphenyl and acenaphthene respectively, are practically identical, but it is worthy of note that the formation of acenaphthene, a substance much less stable than diphenyl, is accompanied by a sensibly greater absorption of heat. The heat of formation of camphene is positive, like that of the paraffins and olefines, whilst the heats of formation of the polyacetylenic hydrocarbons are negative, like that of their generator, acetylene. C. H. B.

* Cx, diamond + Hy gas = $CxHy$ crystallised.

Heats of Combustion and Formation of Carbohydrates. By BERTHELOT and VIEILLE (*Compt. rend.*, **102**, 1284—1286).—The heats of combustion were determined in the calorimetric bomb. The third column gives the heats of formation of the solid compounds from carbon (diamond), hydrogen, and oxygen :—

	Heat of combustion.		
	Constant volume.	Constant pressure.	Heat of formation.
Mannitol, $C_6H_{14}O_6$ ..	+ 728·2	+ 728·5	+ 318·5
Dulcitol, $C_6H_{14}O_6$ ..	+ 729·1	+ 729·4	+ 317·6
Lactose, $C_6H_{12}O_6$ ...	+ 679·9	+ 679·9	+ 298·1
Saccharose, $C_{12}H_{22}O_{11}$	+ 1355·04	+ 1355·04	+ 532·0
Cellulose, $C_6H_{10}O_5$..	+ 681·8	+ 681·8	+ 227·2
Starch, $C_6H_{10}O_5$....	+ 684·9	+ 684·9	+ 224·1
Inulin, $C_6H_{10}O_5$	+ 678·3	+ 678·3	+ 230·6
Dextrin, $C_6H_{10}O_5$ ...	+ 667·2	+ 667·2	+ 241·7

C. H. B.

Heats of Combustion of Fatty Acids and their Derivatives. By W. LOUGUININE (*Comp. rend.*, **102**, 1240—1243).—

	One gram.	Gram-molecule.
Caprylic acid, $C_8H_{16}O_2$	7907·6	1138694
Nonylic acid, $C_9H_{18}O_2$.....	8147·8	1287352
Lauric acid, $C_{12}H_{24}O_2$.....	8798·6	1759720
Myristic acid, $C_{14}H_{28}O_2$.....	9042·0	2061758
Palmitic acid, $C_{16}H_{32}O_2$.....	9264·8	2371794
Trilaurin, $C_3H_5(C_{12}H_{23}O_2)_3$....	8946·19	5707669
Trimyristin, $C_3H_5(C_{14}H_{27}O_2)_3$.	9143·9	6607896

In the acid series the increase in the heat of combustion for each increment of CH_2 is about 153000 cal. per gram-molecule. The combustion of an imperfectly purified specimen of stearic acid gave 2703879 cal. as the heat of combustion, the calculated value from the average difference being 2681830.

The heat of combustion of trilaurin is 36034 cal. greater than the sum of the heats of combustion of glycerol and lauric acid, and in the case of trimyristin the difference is 30167. It would seem, therefore, that the combination of the fatty acids with glycerol, with elimination of $3H_2O$, is accompanied by an absorption of about 30000 cal., in this respect resembling the combination of fatty acids with monohydric alcohols. Applying this relation to tripalmitin and tristearin, the calculated heat of combustion of the former is 7537837, and of the latter 8467945 cal. In the same way the heats of formation and of combustion of the other fats derived from the fatty acids can be calculated. C. H. B.

Heat of Combustion of Coal. By W. ALEXÉEFF (*Ber.*, **19**, 1557—1561).—The researches of Scheurer-Kestner have established that analytical data are inadequate for the determination of the heat

evolved in the combustion of coal. On the other hand, the apparatus used by Fischer, Schwackhöfer and others are too complicated, and the corrections to be applied are too many and too important. In this paper, a simple form of apparatus for this purpose is described, based mainly on the "combustion chamber" used by Berthelot; thermometers divided to $\frac{1}{50}°$ were used, in the reading of which parallax errors were avoided. The sources of error are discussed in full, and the necessary corrections applied for the heat of combustion of the volume of hydrogen used for the ignition of the coal. The result obtained with a sample of South Russian coal gave a value of 7991 cal. per gram. From the analytical data C = 81·4, H = 4·8, O + N = 13·0, and ash 0·73 per cent., the result calculated according to Dulong's rule was 7699 cal., a slightly lower value.

V. H. V.

Density of Liquefied Gases and their Saturated Vapours. By L. Cailletet and Mathias (*Comp. rend.*, **102**, 1202—1207).—The pure and dry gases were introduced at the ordinary temperature and pressure into a strong glass vessel terminating in a graduated glass tube surrounded by a liquid kept at a constant temperature. The volume of the reservoir and tube was accurately known, and hence the weight of the gas introduced could readily be calculated. The gas was compressed until a certain quantity of liquid was formed, and the pressure was then very gradually reduced until the last drop of liquid just disappeared. At this moment the position of the mercury and the temperature were read off, and the volume and pressure of the gas being thus determined, and its weight being already known, the density of the saturated vapour was easily calculated. The following are some of the values obtained:—

Nitrous oxide	Temperature	− 28°	−7·5°	−1·5°	+11·8°
	Density of sat. vapour	0·0378	0·066	0·0785	0·114
	Temperature	+ 20·7°	+28°	+33·9°	
	Density of sat. vapour	0·153	0·202	0·265	
Ethylene	Temperature	− 30°	−23°	−9°	−2°
	Density of sat. vapour	0·0329	0·0389	0·0632	0·0831
	Temperature	+ 3·3°	+6·1°	+8·9°	
	Density of sat. vapour	0·1004	0·123	0·150	
Carbonic anhydride	Temperature	− 23°	− 5°	+0·5°	+10·1°
	Density of sat. vapour	0·057	0·085	0·0983	0·141
	Temperature	+ 19·7°	+30·2°		
	Density of sat. vapour	0·201	0·350		

The apparatus used to determine the density of the liquefied gases consists of a strong glass reservoir and tube attached to a steel reservoir filled with mercury. A horizontal tube is fused to the glass reservoir, and terminates at the other end in two parallel and vertical graduated glass tubes, both of which contain a certain quantity of mercury. The gas is compressed in the reservoir and one of the vertical tubes is cooled. The liquefied gas condenses mainly in the

cooled tube, and a certain quantity is also allowed to form in the other tube in order to avoid any error of capillarity. If h = the difference between the heights of the liquefied gas in the two tubes, h' the difference between the heights of the mercury, δ the density of the mercury, and d the density of the saturated vapour at the particular temperature, then x, the density of the liquid, is obtained by the formula $hx = h'\delta + (h - h')d$. The following are some of the values obtained:—

Nitrous oxide	Temperature	− 20·6°	− 11·6°	− 2·2°
	Density of liquid	1·002	0·952	0·912
	Temperature	+ 11·7°	+ 19·8°	+ 23·7°
	Density of liquid	0·810	0·758	0·698
Ethylene	Temperature	− 21°	− 7·3°	− 3·7°
	Density of liquid	0·414	0·342	0·353
	Temperature	+ 4·3°	+ 6·2°	
	Density of liquid	0·332	0·306	
Carbonic anhydride	Temperature	− 34°	− 25°	− 11·5°
	Density of liquid	1·057	1·016	0·966
	Temperature	− 1·6°	+ 11·0°	+ 22·2°
	Density of liquid	0·910	0·840	0·726

The experiments with ethylene are very difficult on account of the great mobility of the liquid at the higher temperatures, and the values for this gas must, therefore, be taken with some reserve.

The numbers for the density of the saturated vapour of carbonic anhydride agree closely with those calculated by Sarrau by means of Clausius' tables, but the differences between the observed and calculated densities of the liquid are considerably greater.

The graphic representation of the densities of each substance gives two curves which seem to agree at the critical point. In other words the density of the liquid at the critical point is identical with that of its saturated vapour, and this result furnishes a means of determining graphically the density at the critical point when the critical temperature is known. The values thus calculated are, carbonic anhydride − 0·46, nitrous oxide − 0·41, and ethylene − 0·22.

C. H. B.

Specific Volumes at the Boiling Point and other Temperatures. By A. Horstmann (*Ber.*, **19**, 1579—1595).—The more recent investigators have followed the example of Kopp in selecting the boiling point as the temperature for the determination of the specific volumes of liquids, as a point of greatest physical comparability and analogous composition. It has also appeared that at this point the greatest regularities are manifest in the specific volumes of the elements of which the liquids are composed. But as the exceptions become more numerous the wider the experimental field, the author in this paper raises the question how far this selection of the boiling point is justified, and whether the regularities herein observed are not due to fortunate coincidences of favourable conditions. In the first

place, the boiling point varies with the pressure, and, so far as the few experiments show, the volume relations are only similar, not identical at different pressures. Secondly, on theoretical considerations the critical point or absolute temperature would appear to be preferable (compare Mendeléeff, Trans., 1884, 126; and Thorpe and Rucker, *ibid.*, 135), but exact determinations of the former point present considerable difficulty. It is also pointed out that although in many cases the molecular volumes of many isomeric liquids are more nearly equal at their respective boiling points than at lower temperatures, yet this result is far from being general. In many cases the volumes are more nearly equal at points equidistant from their boiling point. Kopp's argument that the boiling point is the most preferable, inasmuch as at that temperature twice the molecular volume of alcohol is equal to the sum of the molecular volumes of ether and water, is criticised, and it is shown that this particular coincidence is rather fortuitous. Tables are also given to illustrate the fact that the differences for every CH_2 added to the molecule are quite as nearly equal if the molecular volumes are compared at zero as at the boiling point. Again, in comparing the molecular volumes of the ketones and aldehydes with those of the alcohols, it is tacitly assumed that the difference is entirely due to the differences in combination of the oxygen-atom only, and not also of the other elements with which it is associated. V. H. V.

Dissociation of Calcium Carbonate. By H. Le Chatelier (*Comp. rend.*, **102**, 1243—1245).—The temperatures were measured by means of the thermo-electric couple previously described. The following results were obtained—

Temperature	547°	610°	625°	740°
Tension of dissociation	27 mm.	46 mm.	56 mm.	255 mm.
Temperature	745°	810°	812°	865°
Tension of dissociation	289 mm.	678 mm.	763 mm.	1333 mm.

The tension of dissociation becomes equal to the atmospheric pressure at about 812°, but if the carbonate is heated rapidly the stationary temperature of decomposition is 925°. A similar phenomenon is observed in the case of gypsum, the stationary temperature being 128°, or 28° above the temperature at which the tension of efflorescence becomes equal to the atmospheric pressure. Calcium hydroxide shows the same peculiarity. The result is due to the slowness with which equilibrium of tension is established in dissociation. By rapid heating, the temperature can be raised beyond the normal temperature of dissociation, but cannot exceed it by more than a limited quantity, because the rate of decomposition increases by a very rapid exponential function of the excess of temperature, so that a point is soon reached at which considerable variations in the rapidity of heating are followed by variations in temperature which are too small to be measured. C. H. B.

Explosion of Homogeneous Gaseous Mixtures. By D. Clerk (*Chem. News*, **53**, 207—209).—In the present experiments a self-registering apparatus was used, and curve records were obtained of the rapidity, intensity, and duration of explosions, temperature, of course, being noted. Mixtures of air with coal-gas and with hydrogen were experimented on. With regard to the value as power producers in gas-engines, the most economical mixture for non-compressive engines was found to be in one case 1 of gas to 11 of air, in another case 1 to 12. Hydrogen gave the lowest values. The results obtained accord with those of previous experiments on the question of the existence of a limit; the heat accounted for by explosion in no case amounted to more than 77 per cent. of the total heat corresponding with the inflammable gas present, and in most cases was but little over 50 per cent. From a study of the records the following conclusions are drawn :—All the phenomena of these explosion curves cannot be accounted for by any single theory previously stated. Mallard and Le Chatelier's theory of increased specific heat of the gases—nitrogen and oxygen—at high temperatures is erroneous. Although dissociation probably occurs to a considerable extent at the higher temperatures, it is not the sole cause of the limitation of the increase of pressure. The combustion is most rapid at first, and decreases in activity as the combination approaches completion. The explosion vessel is entirely filled with flame before the combustion is complete. The limiting causes act after the flame has spread. The limiting causes in weak mixtures are diminution in the rate of burning as the reaction approaches completion and consequent cooling. D. A. L.

Theory of Explosions. By R. Threlfall (*Phil. Mag.* [5], **21**, 165—179).—In these experiments the author explodes under water charges of mercury fulminate enclosed in glass bulbs. The *débris* and products of combustion were found to be projected in a given direction with a peculiar rolling motion of great velocity, which, however, soon comes to rest. It was found that the direction was determined by accidental thicknesses in the glass. Subsequently gauges were used in order to see if the force of explosion took the same direction as the *débris*. This was found to be the case.

From these facts the author considers that at the moment of explosion of the fulminate, a sphere of expanding gases is formed with the firing point at its centre, but that owing to want of symmetry in the position of the latter, the curvature of the sphere becomes distorted, and it finally breaks up into jets of gas which produce vortex motion.

The author then reconsiders the action of detonators, and supports Berthelot's view that a detonator produces in the neighbouring medium a velocity sufficient, if arrested, to produce heat enough to decompose the explosive.

The author considers explosion by influence to be due to vortex motion in, and not to synchronous vibrations of the surrounding medium, since in order to disturb the equilibrium of a molecule by vibrations of the surrounding medium, it is necessary that the vibrations of the medium should be comparable to those of the molecule,

which is hardly possible in the case of air. On the other hand, the peculiar selectiveness which characterises explosions supports the theory of vortex motion. H. K. T.

Explosions of Electrolytic Gas and Volatile Carbon Compounds. By A. Pizzarello (*Gazzetta*, **16**, 161—166).—When electric sparks are passed through electrolytic gas saturated with the vapour of a volatile carbon compound, such as ether, ethyl and methyl alcohols, or ethyl formate, a coloured flame is noticed during the explosion, and a small quantity of carbonic oxide is produced. The results of the experiments described in this paper indicate that if the proportion of the carbon compound is considerable, the sparks tend at first to decompose it, rather than cause the union of the hydrogen with the oxygen. But if the proportion be relatively small, the union of the two gases incites the decompositions of the carbon compound to a greater or less degree. V. H. V.

Principle of Equivalence in Phenomena of Chemical Equilibrium. By H. Le Chatelier (*Compt. rend.*, **102**, 1388—1391).—The author extends the mechanical law of equivalence to chemical phenomena. In all phenomena of equilibrium, two material systems equivalent with respect to a third system, that is, able separately to remain in equilibrium with it, will also be equivalent with respect to any other system to which they may be opposed, and they will likewise be in equilibrium when opposed to one another. As instances of the application of this law to various phenomena, the author cites the fact that the tension of water vapour and of saline solutions is the same at their freezing point as that of ice; the tension of dissociation of chlorine hydrate is the same in presence of ice or of a solution of chlorine at the freezing point of the latter; the coefficients of solubility of two hydrates are the same at the moment of transformation, and the solubility of a substance at its melting point is the same whether it is solid or liquid. The two oxychlorides of antimony at their point of transformation are in equilibrium with the same solution of hydrochloric acid; in cases of double decomposition when the solution becomes saturated with one of the reacting salts, and the latter begins to precipitate, the conditions of equilibrium are not affected because the precipitated salt is equivalent to its saturated solution; the conditions of equilibrium are not altered by "actions of presence," such as the formation of ethereal salts in presence of hydrogen chloride, any apparent modification being due to the fact that the presence of the third body makes it possible to reduce the temperature of the reaction, and thus obtain the limit of combination or decomposition corresponding with the lower temperature.

This law reduces the number of experimental results actually necessary, because it allows a given body in a system in equilibrium to be replaced by its saturated solution, saturated vapour, the products of its dissociation, &c. It also renders it possible to calculate *à priori* all the conditions of equilibrium of the substitution or double decomposition of a system of bodies when the law of dissociation of each of the bodies separately is known.

The action of water vapour on calcium carbonate is discussed in detail as an instance of the application of the law. C. H. B.

Extension of the Law of Solidification. By F. M. Raoult (*Compt. rend.*, **102**, 1307—1308).—The experiments which have hitherto confirmed the author's law "that a molecule of any compound whatever, when dissolved in 100 molecules of any liquid whatever of a different nature, reduces the freezing point of this liquid by an almost constant quantity which approximates to 0·62°," have all been made with solutions in liquids which solidify at temperatures not far removed from the ordinary temperature. The author has now made similar experiments with solutions in thymol, which melts at 48·55°, and in naphthalene which melts at 80·10°.

Organic compounds of all types, and metallic chlorides, dissolved in thymol, produce a molecular reduction of the freezing point which is always practically the same and approximates to 92°. The phenomena are similar to those observed with acetic and formic acids, but the value of the constant is different.

The solution of metallic chlorides and organic compounds (except alcohols and acids) in naphthalene produces a practically constant molecular reduction of the freezing point amounting to 82°. Alcohols and acids produce a molecular reduction of 41°. Solutions of hydroxy-derivatives in benzene, nitrobenzene, and ethylene dibromide, present the same anomaly.

By dividing the molecular reduction by the molecular weight of the solvent, the value obtained for thymol is 0·61, and for naphthalene 0·64. It follows, therefore, that the author's law holds good for all organic solvents whatever the temperature at which they solidify.

C. H. B.

Saturation of Salt Solutions. By W. W. J. Nicol (*Phil. Mag.* [5], **21**, 70—76).—This is a continuation of the author's researches (Abstr., 1885, 340), in which he shows that the solubility of a salt depends on the relation between the cohesion of the salt and the adhesion of water to the salt.

From his results the author obtains by interpolation the formula—

$$\text{Molecular volume} = 1800 + na + n^2\text{B} - n^3y,$$

the constants n, B, and y depending on the salt in question, whence the mean molecular volume or apparent volume of the salt molecule (Thomsen's $\frac{r}{n}$) $= a + n\text{B} - n^2y$.

This operation represents a parabola whose apex is $\frac{\text{B}}{2y}$, and this value is found to represent the solubility of the salt as shown in the following table:—

Salt.	B.	y.	$\frac{B}{2y}$.	Solubility.
NaCl	0·771	0·035	11·0	10·99
KCl	0·738	0·041	9·0	8·38
$NaNO_3$....	0·650	0·018	18·1	18·45
KNO_3	1·254	0·114	5·5	5·63

Moreover the apex represents the point at which saturation takes place, and is such that $a + n\mathrm{B} - n^2y$, or the mean molecular volume, remains the same for any two values of n which are close together, but since a positive change in n is the result of cohesion, and a negative change of adhesion, it is evident that at this point these two forces are in equilibrium.

From results obtained by Rudörff (Abstr., 1885, 865), in which the addition of one constituent to a saturated solution of the double salt causes either complete or partial precipitation of the double salt, the author considers that double salts do not exist as such in solution, and that therefore a saturated solution of a double salt is not necessarily saturated to both its constituents. On continued addition, however, of one of the constituents B, a point is reached at which any one molecule of A may be supposed to be in contact with B, and separation will ensue. If the attraction AB is greater than either AA or BB, then complete precipitation of the double salt will take place if excess of B be added. If not the precipitation will only be partial.

H. K. T.

Relations of Pressure, Temperature, and Volume in Saturated Vapours. By W. C. Unwin (*Phil. Mag.* [5], **21**, 299—308).—The author, after remarking on the absence of any simple and reversible formula connecting pressure, volume, and temperature in a saturated vapour, compares the results obtainable from a formula $\frac{t}{p}.\frac{dp}{dt}$ = constant with those obtained by Ramsay and Young from the arbitrary relation $t\frac{dp}{dt}$ = constant (*Phil. Mag.* [5], **20**, 526). This formula $\frac{t}{p}.\frac{dp}{dt}$ represents the ratio between the total heat of evaporation and the heat expended in external work, and the author considers that this fact is at the basis of the numerous relations obtained.

The author then goes on to show that the formula $\frac{t^2}{p}.\frac{dp}{dt}$ gives still more constant results, and finally the empirical relation $\frac{t^{2\cdot25}}{p}\frac{dp}{dt}$ where t is the absolute temperature, is chosen. This expression is integrable, and gives rise to the following equations:—

$$\log p = a - \frac{b}{t^n} \qquad t = \left(\frac{b}{a - \log p}\right)^{\frac{1}{n}}$$

$$\mathrm{L} = m - \frac{n}{(a - \log p)^{\frac{1}{n}}}$$

where $n + 1$ = the index of t, those calculated for steam from Regnault's data become—

$$\log p = 7{\cdot}5030 - \frac{7579}{t^{1{\cdot}25}}$$

$$t = \left(\frac{7579}{7{\cdot}5030 - \log p}\right)^{\frac{4}{5}}$$

$$\mathrm{L} = 799 - \frac{394}{(a - \log p)^{\frac{4}{5}}}.$$

Equations are also given for alcohol, ether, mercury, and carbonic anhydride. H. K. T.

Determination of Absolute Neutrality. By J. R. Duggan (*Amer. Chem. J.*, 8, 211—222).—These experiments were undertaken in order to compare the action of organic acids and alcohols on soluble ferments with their action on organised ferments, and are a continuation of some former studies on the relation between chemical constitution and physiological action. One of the principal objects was to ascertain whether the action of acids on diastase was proportional to their affinity. By proper purification of the starch and diastase used, the influence of any acid, alkali, &c., added becomes much more marked: thus formic acid of 0·001 per cent. entirely stops the action. That sodium chloride has an acid reaction has been already shown, its effect in accelerating the retarding action of hydrochloric acid on diastatic action cannot however be discerned. Sodium acetate is an alkaline salt, and requires the addition of 1 mol. of acetic acid to render it neutral to diastase.

The following list gives the number of milligrams of the several acids named that must be added to 20 mgrms. of caustic soda after it has been converted into the normal salt, in order to obtain mixtures that all retard the action of diastase to the same extent: Formic acid, 14·4; acetic, 150; propionic, 246; isobutyric, 273; lactic, 27·0; benzoic, 82·4; phenylacetic, 129; oxalic, 6·30; succinic, 109; pyrotartaric, 99·0: malic, 38·5; tartaric, 18·4; fumaric, 18·3; phthalic, 42·5; citric, 46·4. In the case of the monobasic acids these numbers agree very well with those which, according to Ostwald, express the affinities of the acids; the following numbers express the number of milligrams of the several acids that invert the same amount of cane-sugar as does 150 mgrms. of acetic acid: Formic acid, 13·8; acetic, 150; propionic, 255; isobutyric, 286; lactic, 26·1; benzoic, 85; phenylacetic, 125; oxalic, 3·7; succinic, 66·4; pyrotartaric, 57·8; malic, 20·8; tartaric, 10·9; fumaric, 10·9; phthalic, 11·6; citric, 15·7.

Hence the conclusion that the amount of a monobasic acid required to neutralise an "alkaline salt" (*i.e.*, normal salt) of that acid is proportional to its affinity as measured by its action on cane-sugar; in the case of polybasic acids the amount of acid required is larger, and this greater alkalinity of the salts of polybasic acids is no doubt to be attributed to a mutual reaction between the several carboxyl-groups.

7 grams of alcohol to 100 c.c. of solution retards the action of diastase, but the effect is neutralised by addition of 3 mgrms. of acetic acid; no ethyl acetate is however formed. Addition of alcohol also retards the inversion of sugar. The behaviour of alcohol is difficult to explain; alkaline but no basic properties are shown. H. B.

Absorption of Mercury Vapour by Platinum-black. By T. Ihmori (*Ann. Phys. Chem.* [2], **28**, 81—86).—In some previous experiments (Warburg and Ihmori, (*Ann. Phys. Chem.* [2], **27**, 481)) on the absorption of aqueous vapours by platinum-black, the author observed that the presence of a mercury manometer affected the results. In this paper, determinations are made of the amounts of mercury vapour absorbed by various forms of platinum and other metals. The metals are placed on the pan of a very delicate balance, their increase in weight being indicated by the deflections of the pointer. 30 divisions of the scale correspond to 0·0001 gram. The balance case was connected with a mercury manometer, and was exhausted. The following results were obtained:—0·3 gram of platinum-black at an average temperature of 17° increased in weight 0·0021 gram in five hours. It did not regain its absorptive power after being heated to 340° for a quarter of an hour.

0·3 gram of spongy platinum from ammonic platinic chloride at 15—17° increased in two hours by an amount corresponding to 55·5 divisions of the scale.

Platinum and gold foil, after an hour's exposure, showed no increase in weight.

Silver foil of 11·1 sq. cm. area increased in one hour by 2·7 divisions. Experiments by Hittorf (*Ann. Phys. Chem.*, **136**, 3) gave values corresponding to 4·3 divisions.

0·3 gram of finely divided silver, from ammoniacal silver formate, increased in one hour at 16·6° by 46 divisions. Experiments were then made in order to see if by absorption with platinum-black, the spectroscopic lines due to mercury vapour could be made to disappear. They were found to be only weakened.

Finally the author employs the absorptive power of platinum-black to obtain the vapour tension of mercury at ordinary temperatures. For this purpose a globe of known capacity was furnished with two tubes closed by stopcocks, one leading to a small tube containing mercury, the other to the balance case. The latter, after the balance had been charged with 0·25 gram platinum-black, was exhausted, together with the globe, communication with the mercury being cut off. Communication was then closed between the balance and the globe and the mercury stopcock left open for an hour. Lastly the latter was closed, and communication made again with the balance case until the platinum-black ceased to gain weight. The results obtained so far confirm the figures given by Hertz (*Ann. Phys. Chem.* [2], **17**, 193). H. K. T.

Inorganic Chemistry.

Tellurous Anhydride. By D. Klein (*Bull. Soc. Chim.*, **45**, 714—720).—Tellurous anhydride is dimorphous; it crystallises from aqueous solutions in regular octahedra; sp. gr. = 5·65 at 15—19° (compare *Bull. Soc. Chim.*, **45**, 198), and on cooling the fused anhydride, it is obtained in long, rhombic prisms of sp. gr. 5·915 at 0°.

Potassium hexatellurite, $6TeO_2,K_2O + 2H_2O$, may be prepared by mixing aqueous solutions of potassium tellurite (2 mols.) and oxalic acid (1 mol.), filtering, and drying at 100°; it melts at a low red heat. When potassium tellurite is treated with an equal weight of oxalic acid, tellurous anhydride is precipitated.

Indefinite compounds of telluric hydroxide with phosphoric and tungstic acids were also obtained.

Barium telluryl tartrate, $(C_4H_4O_6)_2Ba(TeO)$, is obtained by adding a solution of barium nitrate to a solution of potassium telluryl tartrate (compare this vol., p. 336). A. P.

Phosphorus Oxyfluoride. By H. Moissan (*Compt. rend.*, **102**, 1245—1248).—When a powerful induction spark is passed through a mixture of 2 vols. of phosphorus trifluoride and 1 vol. of oxygen, combination takes place with detonation, and the product occupies 2 vols. The mixture, however, does not explode with a feeble spark, and is not ignited by an ordinary gas flame. In contact with an oxyhydrogen flame it takes fire and burns comparatively slowly. The product, *phosphorus oxyfluoride*, POF_3, is a colourless gas which fumes in the air, and is rapidly absorbed by water, yielding a solution which contains no phosphorous acid. It is also absorbed immediately by alcohol and by solutions of alkalis or of chromic acid. When perfectly dry it has no action on mercury or glass. If heated in a glass tube it decomposes less rapidly than the trifluoride, and there is no deposit of phosphorus, the products being silicon fluoride and an alkaline phosphate. Phosphorus oxyfluoride liquefies under a pressure of 15 atmospheres at 16°, or at −50° under ordinary pressure. If it is compressed under 50 atmospheres and the pressure is suddenly released, it solidifies to a snow-like mass. The density of the gas was found to be 3·68 to 3·75; calculated 3·63.

The existence and mode of formation of phosphorus oxyfluoride is another instance of the tendency of fluorine to form ternary and even quarternary compounds—a property which increases the difficulty of isolating this element. C. H. B.

Phosphorus Pentasulphide. By F. Isambert (*Compt. rend.*, **102**, 1386—1388).—When a solution of phosphorus and sulphur in carbon bisulphide is exposed to sunlight, it deposits a yellowish powder, which, after about a year, crystallises in a confused mass. After the crystals have been washed with carbon bisulphide, in which they are only slightly soluble, they alter and are partially oxidised when

exposed to moist air, and if heated they burn with formation of sulphurous and phosphoric anhydrides. When heated in an inert atmosphere, the crystals melt to an almost colourless liquid, which darkens rapidly as the temperature rises, and distils very slowly at a high temperature. The crystals and the distillate have the composition P_2S_5, and this sulphide is formed under the given conditions even in presence of an excess of phosphorus. The pentasulphide obtained in this way boils at 520°, whilst that prepared by Kekulé's method boils at 518° (Goldschmidt); vapour-density at the softening point of glass 8·0.

Phosphorus trisulphide is obtained readily and without explosion by heating sulphur in a current of carbonic anhydride with the necessary quantity of compact, amorphous phosphorus prepared at a high temperature. It boils at about 490°, and the distillate crystallises in needles resembling those of prismatic sulphur; its vapour-density at a high temperature is 10·2, but at a lower temperature it is greater than 12 (calculated 10·9). C. H. B.

Spectrum and Atomic Weight of Germanium. By L. de Boisbaudran (*Compt. rend.*, **102**, 1291—1295).—The spark spectrum of germanium contains several lines, but two, of wave-length 4680 and 4226 respectively, are especially remarkable. Assuming that germanium is intermediate between silicon and tin, and applying to these lines the author's formula for the relation between atomic weights and homologous lines in spectra, the atomic weight of germanium is calculated to be 72·3. Winkler gives 72·75 as the provisional value. C. H. B.

Potassium and Sodium Peroxides. By H. C. Bolton (*Chem. News*, **53**, 289—290).—When potassium is dropped into molten potassium nitrate the metal burns with a bright light, with the formation of yellowish potassium peroxide which dissolves in the fused mass, imparting to it a deep, rich red colour. In a similar manner sodium and sodium nitrate give rise to a yellowish-red solution, whilst sodium and potassium nitrate give a brown-red solution. In all cases the colour disappears on cooling, but on heating again reappears. The aqueous solutions from the colourless masses give a greenish precipitate with copper sulphate. The action of sodium on fused potassium chlorate is attended with dangerously explosive violence. D. A. L.

Crystalline Form of Sodium Pyrophosphates and Hypophosphates. By H. Dufet (*Compt. rend.*, **102**, 1327—1329).—The sodium salts of pyrophosphoric acid contain the same amount of water of crystallisation as the corresponding salts of hypophosphoric acid.

$Na_4P_2O_7 + 10H_2O$	$Na_2H_2P_2O_7 + 6H_2O$
$Na_4P_2O_6 + 10H_2O$	$Na_2H_2P_2O_6 + 6H_2O$

The author has measured crystals of these compounds, obtained from Joly, with the following results.

Normal Sodium Pyrophosphate.—Monoclinic prism of 76° 16′;

$b : h :: 1000 : 1162{\cdot}606$; D = 789·723; d = 613·464; inclination of the principal axis to the base, 81° 44′.

Normal Sodium Hypophosphate.—Monoclinic prism of 79° 24′; $b : h :: 1000 : 1206{\cdot}980$; D = 774·396; d = 632·700; inclination of the principal axis to the base, 79° 44′.

Disodium Dihydrogen Pyrophosphate.—Monoclinic prism of 61° 8′; $b : h :: 1000 : 906{\cdot}993$; D = 896·717; d = 442·608; inclination of the principal axis to the base, 56° 41′.

Disodium Dihydrogen Hypophosphate.—Monoclinic prism of 63° 38′; $b : h :: 1000 : 906{\cdot}698$; D = 895·551; d = 444·966; inclination of the principal axis to the base, 53° 13′.

The measurements of the normal pyrophosphate agree well with those made by Handl, and those of the normal hypophosphate with measurements by Fresenius.

The author has also determined the sp. gr. of the salts in petroleum.

	Mol. wt.	Sp. gr.	Mol. vol.	Diff.
$Na_4P_2O_7 + 10H_2O$	446	1·824	244·6	9·8
$Na_4P_2O_6 + 10H_2O$	430	1·832	234·8	
$Na_2H_2P_2O_7 + 6H_2O$ ..	330	1·848	178·6	8·0
$Na_2H_2P_2O_6 + 6H_2O$ ..	314	1·840	170·6	

This may not be a true case of isomorphism in the sense in which the word was used by Mitscherlich, but it is a further illustration of the fact that the crystalline form differs but slightly when the percentage composition is practically the same. C. H. B.

Monosodium Arsenate and Monosodium Phosphate. By A. Joly and H. Dufet (*Compt. rend.*, **102**, 1391—1394).—A solution of monosodium phosphate of sp. gr. somewhat higher than 1·5 deposits octahedral crystals of the composition $NaH_2PO_4 + 2H_2O$. The crystals separate spontaneously at +10°, but at +20° they readily form supersaturated solutions. They do not alter when exposed to air, are very soluble in water, melt at 60°, and, if heated in a closed vessel, decompose into water and the hydrate $NaH_2PO_4 + H_2O$, which gradually crystallises in the liquid.

Crystals of the corresponding arsenate, $NaH_2AsO_4 + 2H_2O$, are obtained from a solution of sp. gr. somewhat higher than 1·7. They effloresce when exposed to the air, and form supersaturated solutions more readily than the phosphate.

These two salts are isomorphous, and their crystals have the following properties:—

Monosodium Phosphate.—Rhombic prism of 95° 6′; $b : h :: 1000 : 1157{\cdot}874$; D = 738·121; d = 675·252; plane of the optical axes perpendicular to a'; bisectrix acute, parallel with p; optical sign negative; practically no dispersion; mean index for D 1·46290; observed interior angle of the optical axes 82° 35′, calculated 82° 50′; sp. gr. = 1·915; molecular volume = 81·5.

Monosodium Arsenate.—Rhombic prism of 94° 55′; $b : h :: 1000 : 1181{\cdot}778$; D = 736·786; d = 676·126; plane of the optical axes perpendicular to a'; bisectrix acute, normal to p; optical sign positive; practically no dispersion; mean index for D = 1·50286;

observed interior angle of the optical axes 88° 57′, calculated 89° 11′; sp. gr. = 2·320; molecular volume = 86·2. C. H. B.

Action of Lead Oxide on Ammonium Chloride. By F. Isambert (*Compt. rend.*, **102**, 1313—1315).—When lead oxide acts on ammonium chloride in a vacuum, the liberated gas acquires, after some hours, a maximum tension which remains constant at a given temperature but increases rapidly with an increase of temperature and becomes equal to the atmospheric pressure at 42—46°. On the other hand, if the temperature is reduced from T to t the tension of the gas also diminishes until it reaches the value corresponding with t. If the gas is removed during the course of the experiment, or if a fresh quantity of lead oxide and ammonium chloride is introduced into the apparatus, no difference in the tension of the gas at a given temperature is observed after equilibrium has been re-attained. These facts show that the reaction between ammonium chloride and lead oxide—a reaction which is accompanied by an absorption of heat—is strictly comparable with a phenomenon of dissociation, and is governed by the ordinary laws of dissociation. C. H. B.

Decomposition of Ammonium Salts by Metallic Oxides and Hydroxides. By Berthelot (*Compt. rend.*, **102**, 1354—1357).—A discussion of results previously published by the author and others.

So-called Silver Subchloride. By S. B. Newbury (*Amer. Chem. J.*, **8**, 196—200; compare Abstr., 1885, 956).—Cavillier's method, treatment of silver chloride in ammoniacal solution with chlorine, yields metallic silver, or a mixture of metallic silver and silver chloride; further the formation of silver subchloride is here impossible, since all authorities agree that silver subchloride is decomposed by ammonia.

Finely divided silver is completely converted into the ordinary silver chloride by treatment with cupric chloride. Silver nitrate treated with stannous chloride gives first a precipitate of silver chloride, then one of metallic silver. Silver citrate heated at 100° in hydrogen constantly loses weight, water and carbonic acid being given off; the red solution of the product is always turbid and grey by reflected light; the coloration is evidently due to finely divided metallic silver. The silver subcitrate when extracted with ether gives a tar-like mass containing much free citric acid.

The author concludes that there is no evidence whatever of the existence of such a compound as silver subchloride. H. B.

Effect of the Presence of Magnesia in Portland Cement. By G. Lechartier (*Compt. rend.*, **102**, 1223—1226).—Portland cement containing 20 to 35 per cent. of magnesia sets well and hardens with lapse of time, but after some time it undergoes considerable expansion, and this expansion takes place with almost irresistible force, shifting foundations, displacing columns, and producing other effects of a similarly destructive character. This result is due to the presence of magnesia, which at first undergoes very little change, but after-

wards absorbs water and becomes hydrated in the manner described by Deville. These conclusions are based on the examination of a large number of cements prepared by different makers and used by different architects and builders for a variety of purposes. The results were the same in all cases. C. H. B.

Some Crystallised Arsenates. By Coloriano (*Bull. Soc. Chim.*, **45**, 709—714).—By treating zinc with excess of arsenic acid and heating the filtered solution at 100°, a white jelly is precipitated which by further heating with water, is transformed into the compound $ZnHAsO_4 + H_2O$. This crystallises in the rhombic or in the monoclinic system, and has already been obtained by different methods by Debray and by Demel. When heated with water, adamite is formed, and not the compound described by Demel.

When the liquid obtained by heating manganese carbonate with an aqueous solution of arsenic anhydride is boiled, a rose-coloured jelly is deposited which is rapidly converted into a crystalline mass having the composition $MnHAsO_4 + H_2O$; this has already been obtained by Debray. When boiled with a further quantity of water for 20 hours it is converted into the compound $(As_2O_5)_2,5MnO,5H_2O$, which forms prismatic crystals; if, however, the digestion be conducted in sealed tubes at 150° for six hours, the compound, $(As_2O_5)_2,5MnO,2H_2O$, is formed; this crystallises in small mono- or tri-clinic prisms.

The compound $CuHAsO_4 + H_2O$, prepared by Debray by digesting with a further quantity of water the liquid obtained by treating cupric carbonate with arsenic acid at 70°, may also be obtained in the cold: by further digesting it with water at 100°, olivenite is formed. A. P.

Preparation of Cuprous Chloride. By A. Cavazzi (*Gazzetta*, **16**, 167—168).—Cuprous chloride can be conveniently prepared by heating a mixture of copper sulphate (4 grams) and sodium hypophosphite (2 grams) in about 50 c.c. of water to which 30 drops of fuming hydrochloric acid are added.

The cuprous chloride is deposited, and can be purified in the ordinary way. The change can be explained thus:—Copper hypophosphite is at first formed, and this is converted by the hydrochloric acid into cuprous chloride and phosphoric acid. The equation is as follows:—$2CuCl_2 + H_3PO_2 + H_2O = H_3PO_3 + 2HCl + Cu_2Cl_2$. V. H. V.

Basic Cupric Arsenate. By Coloriano (*Bull. Soc. Chim.*, **45**, 707—709).—A basic cupric arsenate, $As_2O_5,3CuO$, may be obtained by heating 2 grams of metallic copper with 4·5 grams of arsenic anhydride dissolved in 32 c.c. of water at 180—200° in a sealed tube for 18 hours.

Aphanesite commences to lose water at 290°, but this is not completely removed even at the temperature of boiling sulphur. From his analyses of this mineral the author adopts the formula

$$As_2O_5,6CuO,3H_2O \text{ or } AsO_4(Cu{\cdot}OH)_3.$$ A. P.

Cerium Molybdate. By A. Cossa (*Compt. rend.*, **102**, 1315—1316; compare this vol., p. 595).—When solutions of equivalent quantities of cerous sulphate and sodium molybdate are mixed at the ordinary temperature, a white, gelatinous precipitate is formed, which soon becomes yellow and crystalline. This precipitate is normal cerous molybdate, $CeMoO_4$, and if fused in an inert atmosphere it forms octahedral crystals of sp. gr. 4·56, isomorphous with wulfenite. This method of preparation is similar to that by which the author previously obtained crystallised didymium molybdate; it is quite distinct from Didier's method (*loc. cit.*). C. H. B.

An Aluminium Alloy. By Bourbouze (*Compt. rend.*, **102**, 1317).—An alloy obtained by melting 10 parts of tin with 100 parts of aluminium is more easily worked and is less affected by reagents, &c., than pure aluminium. Moreover it can be soldered as easily as brass without any special preparation. Its sp. gr. is 2·85. C. H. B.

Action of Hydracids on Vanadic Acid. By A. Ditte (*Compt. rend.*, **102**, 1310—1312).—When hydriodic acid is added to a warm solution of red vanadic acid, a deep green precipitate of a less soluble variety is produced, and iodine is liberated. The precipitate dissolves on boiling with excess of hydriodic acid, and iodine vapour is given off, but the liquid still contains free iodine, which can be removed by agitating with finely divided silver. The clear liquid then has a greenish-blue colour which becomes deeper on evaporation, and eventually changes to dark brown, the liquid depositing almost black, deliquescent needles of the composition $V_2O_3I_2,3HI + 10H_2O$. If these crystals are left for several days in a dry vacuum, they lose hydrogen iodide, cease to fume in the air, and are converted into the compound $V_2O_3I_2,2HI + 8H_2O$. These compounds are derivatives of hypovanadic oxide, formed as a result of the reactions $V_2O_5 + 2HI = V_2O_4 + 2H_2O + I_2$ and $V_2O_4 + 2HI = V_2O_3I_2 + H_2O$. They are very soluble in water, and the solutions give with excess of ammonia, a dark-green precipitate, which dissolves in pure water but is insoluble in presence of ammonium salts. When dissolved in boiling water this precipitate yields a dark-green solution, which deposits small, green crystals of the composition $V_2O_4,2(NH_4)_2O$. The solution oxidises when exposed to the air and becomes colourless, normal ammonium vanadate being formed.

Hydrobromic acid when added to a concentrated solution of red vanadic acid produces a yellow, flocculent precipitate of a less soluble variety, but this dissolves when gently heated with excess of hydrobromic acid, forming a deep greenish-brown solution containing free bromine, which is expelled by boiling. If the greenish-blue liquid is concentrated by evaporation in a vacuum over potash, it deposits dark green, highly deliquescent crystals of the composition $V_2O_3Br_2,2HBr + 7H_2O$. They dissolve in water, yielding a solution which is greenish-blue when dilute, and dark green when concentrated; with ammonia it behaves like the iodine compound.

Hydrochloric acid produces a yellow precipitate of less soluble vanadic acid, but this dissolves when heated with excess of hydro-

chloric acid, chlorine being liberated, and a pale yellow solution formed. When concentrated by evaporation, the solution becomes deep brown, and deposits small dark-green crystals which, when dried over potash in a vacuum, have the composition $V_2O_3Cl_2 + 4H_2O$. They form a green solution with water. C. H. B.

Austrium, a New Metallic Element. By E. Linnemann (*Monatsh.*, **7**, 121—123).—This substance was isolated as follows from the Arendal orthite. The mineral was extracted with hydrochloric acid, and after removal of lead, copper, tin, and arsenic by treatment with hydrogen sulphide, was neutralised as nearly as possible or mixed with sodium acetate and then again treated with hydrogen sulphide, when it yielded a precipitate containing copper, lead, zinc, cadmium, thallium, iron, calcium, magnesium, and austrium. This precipitate was dissolved in hot hydrochloric acid, treated with excess of soda, filtered, the filtrate gently heated and precipitated with sodium sulphide, and the precipitated sulphides filtered off. The austrium remains in solution, and on exposure to air is partly precipitated as carbonate (mixed with sulphur), partly remains in solution; from this it is obtained by acidifying with acetic acid, evaporation to dryness, solution in water and treatment with hydrogen sulphide, by which it is partially precipitated; the filtrate is again treated in like manner. The precipitates so obtained are still contaminated with copper, lead, and zinc; the separation of the last being especially difficult. The spectrum of the metal is characterised by two lines in the violet α of $\lambda = 4165$, β of $\lambda = 4030$. No description of the metal or of its reactions is given. A. J. G.

Mineralogical Chemistry.

Arsenolamprite. By C. Hintze (*Zeit. Kryst. Min.*, **11**, 606—608).—Analyses of two specimens of a mineral with metallic lustre, from Copiapo in Chili, gave the following results:—

	As.	Fe.	SiO_2.	Total.	Sp. gr.
I	98·14	0·92	0·55	99·61	5·22
II	98·43	1·00	0·05	99·48	5·42

The mineral is evidently native arsenic. The sp. gr. shows that it is the modification to which the unsuitable name of arsenic glance was formerly assigned. The ordinary rhombohedric arsenic has a sp. gr. of 5·7 to 5·8. The other physical properties also induce the author to regard arsenic glance as an independent mineral; and on account of the characteristic metallic lustre of this lighter and softer modification of arsenic, he suggests for it the name of arsenolamprite. B. H. B.

Physical Properties of Graphite. By H. Sjögren (*Jahrb. f. Min.*, 1886, ii, Ref., 23—24).—The author has examined crystals from the limestone of Ceylon and from Pargas in Finland, and artificial graphite from Swedish ironworks. The nature of the twinning, together with the etching figures, and the melting curve, make it probable that graphite crystallises in the hexagonal system.

B. H. B.

Notes on Gold. By A. Leibius (*Jahrb. f. Min.*, 1886, ii, Ref., 28; *J. Royal Soc. New South Wales*, **18**, 37—41).—Towards the end of 1882, rich auriferous deposits were discovered in Queensland, 25 miles from Rockhampton, near the Dee River. The matrix is a ferruginous quartz, in which the gold is disseminated in a very finely divided state. The rock appears to have been deposited from a hot spring, which held the quartz, iron, and gold in solution, and from which the gold has been precipitated. In the cavities opened out in the mine, there hang stalactites of oxide of iron and quartz, containing finely disseminated gold. The gold is remarkable for its purity. It assays 99·7 per cent. of gold; the rest is copper with a trace of iron (compare this vol., p. 21). B. H. B.

Some New South Wales Minerals. By A. Liversidge (*Jahrb. f. Min.*, 1886, ii, Ref., 28—29; *J. Royal Soc. New South Wales*, **18**, 43—48).—*Native gold* is found in association with antimonite at Sandgate, Sandon Co., New England. At the Reform Gold Mining Company, Lucknow, native gold occurs with native arsenic in calcite.

Tourmaline in very fine crystals, resembling those of Bovey Tracy, is found at Uralla.

Scheelite occurs in massive lumps in association with molybdenite and molybdenum ochre at Hillgrove, Sandon Co.

Axinite has been found near Nundle in large, well-formed, brown crystals.

Idocrase has been found in the same district, of a green colour, associated with lime-alumina garnets.

Ironstone concretions are found in the bed of the Macquarie River, at Dubbo. The outer shell consists of soft, brown, hydrated ferric oxide; the interior being filled with sand. The nodules are evidently of quite recent origin.

Lithomarge, of a pale blue colour, occurs as the matrix of the native copper at the Great Blayney Mine, near Blayney.

Chrome iron ore occurs at Nundle as a vein 40 feet thick, in serpentine, diallage rock, and black shales.

Iron pyrites concretions occur at the Sunny Corner Silver and Gold Mine, near Rydal. They resemble septaria, the fissures being filled with marcasite or quartz. B. H. B.

Argyrodite, a New Silver Ore. By A. Weisbach (*Jahrb. f. Min.*, 1886, ii, Mem., 67—71).—This ore was found in September, 1885, in the Himmelsfürst Mine, near Freiberg. It has a metallic lustre, and steel-grey colour. H. = 2·5; sp. gr. 6·085. It is opaque and brittle. It occurs in crystals and in compact masses. The

crystals are monoclinic, $a : b : c = 1 : 1{\cdot}67 : 0{\cdot}92$; the usual form exhibiting the planes ∞P, $\breve{P}\infty$, $-\breve{P}\frac{2}{3}$, $6\breve{P}\infty$, $\frac{1}{3}\breve{P}\infty$. The minerals associated with argyrodite are: spathic iron ore, zinc-blende, galena, copper pyrites, iron pyrites, marcasite, argentite, pyrargyrite, polybasite and stephanite.

A number of analyses gave 75 per cent. of silver and 18 per cent. of sulphur, and a loss of 7 per cent. This loss was found by C. Winkler, on February 1st, 1886, to be due to the presence of a new element, which he called germanium (compare this vol., p. 421, and Proc., 1886, 197). B. H. B.

Carbonates from the Coal-measures. By E. Weiss (*Jahrb. f. Min.*, 1886, ii, Ref., 26).—1. *Ankerite* from the Camphausen Colliery, Saarbrücken. White, lustrous crystals; H. 4; sp. gr. 2·9404. Analysis gave—

FeO.	MnO.	CaO.	MgO.	CO_2.
9·47	1·63	29·77	14·21	45·28

Formula: $10MgCO_3 + 15CaCO_3 + 4(Fe,Mn)CO_3$.

2. *Pistomesite* from the same colliery. Brownish crystals; H. less than 4; sp. gr. 3·442. Analysis gave—

FeO.	MnO.	CaO.	MgO.	CO_2.
36·38	2·03	1·85	17·39	42·56

Formula: $MgCO_3 + FeCO_3$.

3. *Dolomite* from the Vollmond Colliery in Westphalia. Concretions, resembling carbonaceous sphærosiderite, and containing well-preserved plant remains. Analysis gave—

CaO.	MgO.	CO_2.	FeO.	Fe_2O_3.	Iron pyrites.
28·4	18·8	42·7	0·1	0·1	2·6

B. H. B.

Olivine from the Isle of Bourbon. By A. Lacroix (*Zeit. Kryst. Min.*, **11**, 637).—The volcanic sand of this island consists for the most part of olivine crystals, 2 to 4 mm. long, with the planes $\infty\breve{P}\infty$, $\breve{P}\infty$, $2\breve{P}\infty$, $\infty\breve{P}2$ predominating. The crystals are of a yellow colour. Sp. gr. 3·364. Analysis gave—

SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	Total.
39·96	2·33	6·28	2·05	49·18	99·80

The crystals, which frequently contain inclusions of magnetite, are associated with greenish-black crystals of augite, 1 to 5 mm. long.

B. H. B.

Chemical Composition of Menilite. By A. Damour (*Zeit. Kryst. Min.*, **11**, 640—641).—The results of the analyses of the mineral resembling menilite from Ablon (this vol., p. 316) induced the author to analyse the menilites from the gypsum in the vicinity of Paris. The analyses gave—

	Ménil-montant.	Villejuif.	Argenteuil.	St. Ouen.	Monteeau.	Chau-mont.
SiO_2 ..	76·00	78·25	74·50	75·47	67·09	59·10
Al_2O_3 ..	1·10	0·60	1·55	0·15	—	1·40
Fe_2O_3 ..	2·50	0·90	0·45	0·70	0·80	6·60
MgO ..	6·79	8·28	10·30	8·83	9·00	8·71
CaO ..	1·40	0·76	1·22	2·89	8·20	4·10
CO_2 ...	—	0·59	0·94	2·30	—	3·22
H_2O ..	11·70	10·44	9·60	9·50	14·50	16·40
Totals .	99·49	99·82	98·56	99·84	99·59	99·53
Sp. gr..	2·17	2·18	2·16	2·16	2·22	2·25

The author is of opinion that the magnesia, like the calcium carbonate, does not belong to the composition of the mineral, but to mechanical inclusions; the marl in which the menilite nodules occur containing a considerable amount of magnesia. B. H. B.

Oligoclase and Andesine. By A. Des Cloizeaux (*Zeit. Kryst. Min.*, **11**, 641—654).—In the same way as in his monograph on albite (this vol., p. 210), the author communicates at great length the results of his investigations on oligoclase and andesine. He shows that the green oligoclases of Bodenmais, Orijärfvi, and Tilasinwuori, are to be regarded as andesine, *i.e.*, as Ab_1An_1 (oxygen ratio 1 : 3 : 8), a compound regarded also by Wiik as a distinct member of the felspar group. As normal oligoclase, the author regards those plagioclases, with an oxygen-ratio of 1 : 3 : 9 and an extinction of 1° to 6°, generally 2° to 4°, positive. In these plagioclases a plane perpendicular to the axial plane bevels the obtuse edge, and forms with the basal plane an angle of 98° to 104°. Anomalous oligoclases are $0P : \infty\breve{P}\infty$ felspars approaching albite ("oligoclase-albites" = Ab_3An_1 to Ab_5An_1), in which the plane perpendicular to the axial plane cuts the acute edge $0P : \infty\breve{P}\infty$, and forms an angle of 93° with the basal plane. The axial plane consequently is inclined 83° towards $\infty\breve{P}\infty$; extinction angle + 6° to + 12°. A second class of anomalous oligoclases are those in which the axial plane is parallel to 0P or perpendicular to $\infty\breve{P}\infty$, with an extinction angle of + 6° to + 9°. With reference to the position of the plane of the optic axes, the normal oligoclases follow as the third class; and as the fourth class, the andesines. In these, the plane perpendicular to the axial plane forms an angle of 110° to 120° with the basal plane, so that the axial plane is inclined 74° to 64° towards $\infty\breve{P}\infty$. The extinction angle varies from 1° to 10°. In the same plate, however, the extinction is sometimes positive, and sometimes negative.

B. H. B.

New Type of Pyroxene. By K. de Chroustchoff (*Jahrb. f. Min.*, 1886, ii, Ref., 43—45).—The author describes several varieties of tachylite from the Rossberg, near Rossdorf. The augite from one of these glasses is well crystallised; the usual forms being ∞P, $\infty P\bar{\infty}$, $\infty P\breve{\infty}$. The index of refraction was found to be 1·599, and the extinction angle 39°. The composition of this augite (dried at 200°) is as follows :—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Na_2O.	K_2O.	Total.	Sp. gr.
49·18	2·15	4·96	9·04	20·30	13·07	1·89	0·30	100·89	3·434

B. H. B.

A Series of Diopside Varieties from Nordmarken. By G. FLINK (*Zeit. Kryst. Min.*, **11**, 449—487).—The material for this investigation consisted of two varieties of diopside from Nordmarken, the black variety described by H. Sjögren (Abstr., 1881, 380), and the yellow variety described by J. Lehmann (*Zeit. Kryst. Min.*, **5**, 532). These are named by the author, type I and IV respectively. There were also two intermediate varieties, type II and III, and, lastly, a peculiar variety, type V, not included in the known series. With the exceptions of the so-called hedenbergite and a black diopside from Arendal, type I is, of all the diopsides known, the richest in iron. The diopsides from Nordmarken form an uninterrupted series according to their percentage of iron, gradually decreasing from type I to type V, which is one of the diopsides poorest in iron. There are, it is true, older analyses of varieties which are almost entirely free from iron (*e.g.*, salite, white malacolite from Malsijö), and of whose crystalline form nothing is known. But typical diopsides, with the lowest percentage of iron, which occur in good crystals, resemble type V. Of the 22 forms observed, only seven are common to all the varieties. The following six forms are new for diopside: $\infty\breve{P}5$, $\infty\breve{P}7$, $\frac{3}{4}\breve{P}\infty$, $-2\breve{P}\infty$, $-\frac{1}{9}P$, and $\frac{1}{5}\breve{P}\infty$. The form of the crystals appears to change with the change in the percentage of iron. The other characters which vary with the chemical composition are shown in the following table:—

	Type I.	Type II.	Type III.	Type IV.	Type V.
Composition. $CaMgSi_2O_6$	40·9	66·9	84·8	86·7	90·8
$CaFeSi_2O_6$	57·5	31·1	13·8	12·4	9·0
$MgAlSi_2O_6$	1·6	2·0	1·4	0·9	0·2
Axial ratio, *a*-axis	1·09123	1·09178	1·09186	1·09220	1·09197
„ *c*-axis	0·58428	0·58562	0·58659	0·58688	0·58693
Angle of the zone of the β	74° 34′	74° 19′	74° 16′	74° 13′	74° 12′
ortho-axis μ	74 22	74 32	74 32	74 35	74 34
Prism angle	46 27	46 25	46 25¾	46 25½	46 25¼
Colour	black	dark green	grass-green	yellowish-green	white
Extinction angle	44° 38′	44° 41′	39° 1′	38° 45′	38° 3′
Angle of the optical axes for green	60 29	59 6	58 47	58 46	58 40
„ „ „ yellow	60 36	59 11	58 56	58 57	58 52
„ „ „ red	60 44	59 18	59 6	59 9	59 9
Angle between the *c*-axis and bisectrix for green	*x*	41 37	38 55	38 38	37 54
Angle between the *c*-axis and bisectrix for yellow	44° 38′	41 41	39 1	38 45	38 3
Angle between the *c*-axis and bisectrix for red	*x* + 7½	41 47	39 7	38 54	38 11
Refraction index β for green	1·72983	1·71062	1·70029	1·69781	1·69869
„ „ yellow	1·72428	1·70467	1·69588	1·69593	1·69359
„ „ red	1·71659	1·70055	1·68889	1·69133	1·68978

B. H. B.

Schefferite from Långban and Pajsberg. By G. Flink (*Zeit. Kryst. Min.*, **11**, 487—506).—The name schefferite was applied by Mikaelson to a new augite variety from Långbanshyttan. The author is of opinion that the old crystallographical data regarding this mineral are not trustworthy. His analysis gave the following results:—

SiO_2.	CaO.	MgO.	MnO.	FeO.	Total.
52·28	19·62	15·17	8·32	3·83	99·22*

These results differ considerably from the results of the old analyses of Mikaelson and Winkler. The author has also analysed the variety of schefferite from Pajsberg, described as black iron-schefferite (I), and the brown iron-schefferite (II) from Långban, with the following results:—

	SiO_2.	CaO_2.	MgO.	FeO.	MnO.	Al_2O_3.	Total.
I....	50·88	12·72	9·08	17·48	6·67	1·97	98·80
II....	52·19	14·57	10·93	14·98	6·20	0·88	99·75

The results of the author's investigation are briefly as follows:—

The term "schefferite" should be applied to the monosymmetric varieties of pyroxene, the composition of which is characterised by a relatively high percentage of manganese. The crystals of schefferite proper are usually twinned along $\infty\breve{P}\infty$, and extended in the direction of the zone $\breve{P}\infty : P : \infty\breve{P}\infty$, or flattened in the direction of the orthodoma $\breve{P}\infty$, but extremely rarely with a columnar development in the direction of the vertical zone, like ordinary pyroxene. According to its angular dimensions, schefferite resembles the diopside varieties poor in iron. The angles of the optic axes are much greater with schefferite than with ordinary pyroxene. The extinction angle in the plane of symmetry is about the same as that of a diopside rich in iron. The iron schefferites are characterised not only by their composition but also by the general occurrence of the extremely rare pyramid $\frac{1}{2}P$, and by a very large extinction-angle (69°).

B. H. B.

Rhodonite from Pajsberg and Långban. By G. Flink (*Zeit. Kryst. Min.*, **11**, 506—530).—The author has made a careful investigation of the geometrical and optical properties of Swedish rhodonite crystals. He has observed 29 forms, of which number 19 are new.

Discussing the relations between the chemical composition and the optical properties of the pyroxenes described (see the two preceding Abstracts), the author shows that the percentage of iron in diopside effects a morphotropic action in such a way that the angle β becomes greater. The increase in this angle, it is true, is only 0° 22′. It is, however, so regular, that it cannot be accidental. The investigation of schefferite and of rhodonite shows that the percentage of manganese in the diopside formula effects an action exactly opposite. The decrease in the angle β with an increase in the percentage of manganese is considerable. The angle in question is 74° 11′ with

* 99·29 in original.

diopside (free from manganese), 73° 53′ with schefferite (8·32 per cent. of MnO), and 71° 15¾′ with rhodonite (41·88 per cent. of MnO). A relatively low percentage of manganese only lessens the angle β, whilst when the percentage reaches a certain amount, the substance becomes asymmetric. It is not yet known at what percentage of manganese this change in the crystalline system takes place. It is, however, probable that in nature several intermediate members exist between schefferite and rhodonite.

The angle of the optic axes is increased by the percentage of iron. The percentage has the same action. The following are the angles of the optic axes of diopside, schefferite, and rhodonite :—

Type V.	Type I.	Schefferite.	Rhodonite.
58° 52′	60° 36′	65° 3′	76° 12′

The bisectrix of the rhodonite angle is negative, whilst the bisectrices of the other members are positive. B. H. B.

Allanite and Gadolinite. By L. G. Eakins (*Chem. News.*, **53**, 282).—The minerals described are from "Devil's Head" Mountain, Douglas Co., Col., U.S.

Allanite (I) occurs in a round mass of more or less decomposed granite. It is of a pitch-black colour, with a brilliant glossy lustre, and a subconchoidal fracture. Under the microscope the interior appears pale greenish-yellow with irregular fissures. It is isotropic, frequently with a chestnut to strong yellowish-brown, pleochroic, strongly double refractive zone about the kernel. This outer zone is identical in behaviour with the allanite of eruptive rocks. There is evidence of prismatic forms which indicate that the amorphous state is in this case probably a secondary one. Sp. gr. = 3·52 at 29°; H. about 6. Heated before the blowpipe it swells up considerably. It is readily decomposed by acids.

Of gadolinite two specimens were examined. II. Water-worn with smooth fracture exposing a black, slightly lustrous surface, but apparently without cleavage. Under the microscope dark-green and isotropic; whilst the section was fissured and contained films and

	SiO_2.	Al_2O_3.	Fe_2O_3.	Ce_2O_3.	$(LaDi)_2O_3$.	ThO_2.	Er_2O_3.
I ..	31·13	11·44	6·24	12·50	10·98	—	—
II ..	22·13	2·34	1·13	11·10	21·23	0·89	12·74
III ..	21·86	0·54	3·59	6·87	19·10	0·81	15·18

	Y_2O_3.	FeO.	BeO.	MnO.	CaO.	MgO.	K_2O.
I ..	—	13·59	0·27	0·61	9·44	0·16	trace
II ..	9·50	10·43	7·19	—	0·34	0·14	0·18
III ..	12·63	11·36	5·46	0·11	0·47	0·16	0·20

	Na_2O.	H_2O.	CO_2.	P_2O_5.
I	0·56	2·78	0·21	trace
II	0·28	0 86	—	—
III	0·32	0·74	—	—

flakes of dark reddish-brown oxides. It glows brilliantly before the blowpipe. Sp. gr. 4·56 at 17°; H. 6—6·5.

III. Was not water-worn nor was it as dark in colour as specimen (II), even approaching dull-green in places. Sp. gr. 4·59 at 25·5°; H. about 6.

Didymium absorption-line very strong in specimen II, gadolinite. In analyses II and III, Er_2O_3 and Y_2O_3 were calculated by Bahr and Bunsen's formulæ. The absorption-spectrum of erbium from 1 gram of the gadolinite in a solution 2 cm. thick and 1 cm. deep was so weak that the band in the green only was visible. Compared with European specimens from Ytterby and Hitteroe, these specimens of gadolinite contain less Y_2O_3 but more $(Ce,La,Di)_2O_3$, and in addition contain Al_2O_3, ThO_2, Na_2O, and K_2O, which do not occur in the European specimens. D. A. L.

Minerals of the Oolitic Iron Ore of the Windgällen. By C. Schmidt (*Zeit. Kryst. Min.*, **11**, 597—604).—The upper jurassic oolitic iron ore, occurring between the two Windgällen in the canton of Uri, is composed for the most part of flattened elliptical grains, the cement being a mixture of carbonates with grains of red and brown hæmatite and magnetite. The elliptical grains consist of magnetite and a bright green, slightly dichroic mineral; an analysis of 1·0117 gram of which gave the following results:—

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	H_2O.	CO_2.	Total.
I ..	22·81	1·11	18·06	2·58	36·55	1·49	4·28	11·67	0·76	99·31

The substance analysed consisted of 90·43 per cent. of a silicate, 3·12 per cent. of a carbonate, and 5·75 per cent. of ore; the calculated composition of the silicate being—

	SiO_2.	Al_2O_3.	FeO.	MgO.	H_2O.	Total.
II ..	25·23	19·97	37·51	4·39	12·90	100·00

The formula is: $(FeMg)_3Al_2Si_2O_{10} + 3\frac{1}{2}H_2O$, which is analogous to that given by Janovsky (Abstr., 1875, 1165) for chronstedtite. The so-called chamosite from the oolitic iron ores of Chrustenic gave on analysis the following results, after subtracting 5·52 per cent. of carbonate:—

	SiO_2.	Al_2O_3.	FeO.	MgO.	H_2O.	Total.
III...	25·60	18·72	42·31	2·13	11·24	100·00

The mineral is thus very similar to that from the Windgällen described above. A comparison of analyses II and III with Rammelsberg's analyses of chronstedtite and thuringite, shows that these two minerals belong to the same group as Berthier's chamoisite.

In conclusion the author describes a number of secondary minerals occurring in the abandoned iron mines of the Windgällen. The minerals are—quartz, albite, chlorite, calcite, ankerite, spathic iron ore, iron glance, braunite, and iron pyrites. B. H. B.

Porphyritic Hyperite from California. By K. de Chroustchoff (*Jahrb. f. Min.*, 1886, ii, Ref., 57).—This rock, from San Diego,

California, contains porphyritic crystals and fragments of a felspar (oligoclase-albite, Ab_5An_1). The rock also contains disseminated grains of augite and hypersthene, with small quantities of hornblende and biotite as accessory constituents. The ground-mass consists of grains of plagioclase and pyroxene. B. H. B.

Organic Chemistry.

Changes effected in Ethylene by Heat. By D. T. Day (*Amer. Chem. J.*, 8, 153—167).—The action of a definite but low degree of heat on ethylene has not been studied. The gas was prepared from alcohol, thoroughly purified and dried, and placed in a glass tube bent twice at right angles, the open ends being closed by mercury. The middle portion was heated in a small furnace, as was also the bulb of an air thermometer, the mercury in whose pressure gauge served to regulate the supply of gas to the furnace. Ethylene may be heated at 344° for several hours continuously without change of volume or of odour. At 350—355° the gas slowly suffers contraction, amounting to about $\frac{1}{20}$, and acquires an odour of impure kerosene; it is free, however, from marsh-gas or hydrogen, and the new product is, therefore, a simple condensation product. Heated at 400—408° for 171 hours the contraction amounted to a little more than one-half, and a few drops of liquid were formed. This combined readily with bromine, and was free from benzene; the residual gas was free from hydrogen, and contained in 62·7 volumes: ethylene hydrocarbons, 15·6; ethane, 24·8; methane, 22·3. At 450° ethylene is more rapidly acted on, the action ceasing after 72 hours; a very slight amount of carbon is deposited; 55·67 volumes of the residuary gas containing ethylene hydrocarbons, 15·37; ethane, 35·6; methane, 4·7.

H. B.

Selenio-carbon Compounds. By H. Stolte (*Ber.*, **19**, 1577—1579).—*Methyl seleniocyanate*, MeSeCN, obtained from potassium seleniocyanate, and methyl iodide in methyl alcohol solution, is a pale yellow oil, boiling at 158°, insoluble in and heavier than water.

As all attempts to prepare sodium seleniocyanurate in a pure state from sodium selenide and cyanuric chloride were unsuccessful, the product of the reaction was treated with methyl iodide, and the corresponding *methyl* compound, $C_3N_3Se_3Me_3$, obtained. It separates in golden flocculæ, melting at 174°, and can be crystallised from alcohol.

Monophenyl seleniocarbamide, $NH_2{\cdot}CSe{\cdot}NHPh$, prepared from phenyl cyanamide and hydrogen sulphide, forms white crystals, melting at 182°. V. H. V.

Combination of Methyl Alcohol with Barium Oxide. By De Forcrand (*Compt. rend.*, **102**, 1397—1399).—Barium monoxide

dissolves in methyl alcohol with considerable development of heat, and the solution saturated at 15° has a sp. gr. of 1·045, and contains 200 grams of barium oxide per litre. The liquid does not become turbid when mixed with a small quantity of water. If the solution is evaporated at 135° in a current of hydrogen, it yields a mass of white, nacreous plates of the composition 4MeOH,3BaO, analogous to, if not identical with, the compound 2MeOH,BaO, described by Dumas and Peligot (*Ann. Chim. Phys.*, **58**, 17), and quite different from the ethoxide, $Ba(EtO)_2$, formed with ethyl alcohol. The heat of formation was determined by dissolving the compound in hydrochloric acid,

4MeOH liquid + 3BaO solid = 4MeOH,3BaO solid, develops + 62·5 cal.

The heat of formation of barium methoxide would be about + 15·34 cal. The heat of formation of this alcoholate is higher than that of the hydroxide, but if a large quantity of water is added to the solution in methyl alcohol, the hydrate, BaO + $10H_2O$, is precipitated in crystalline plates, its heat of formation being + 42·0 cal.

C. H. B.

Koumiss. By H. W. Wiley (*Amer. Chem. J.*, **8**, 200—206).—For the manufacture of koumiss, cow's milk may be used in place of mare's milk if the greater portion of the cream is first removed; as mare's milk contains 5·3—7·26 per cent. of milk-sugar, and cow's milk only 4·8 per cent., it is sometimes advisable to add some milk-sugar to the latter.

The mean composition of eight samples of koumiss from mare's milk is given by the author as: carbonic anhydride, 0·83; acidity, as lactic acid, 0·47; alcohol, 0·76; nitrogen, 0·449; albuminoïds, 2·56; fat, 2·08; milk-sugar, 4·38; water, 89·32. These samples prepared in Indianopolis thus contain less alcohol and more fat than samples that have been analysed previously.

H. B.

Oxidation of Mannitol. By F. Iwig and O. Hecht (*Ber.*, **19**, 1561—1563).—In answer to Dafert's criticisms (this vol., p. 608), it is shown that the different results obtained by the authors and by Dafert are entirely due to differences in the conditions under which the reaction was studied. Thus with moderate oxidation lævulose is formed: $OH\cdot CH_2\cdot[CH\cdot OH]_4\cdot CH_2\cdot OH + O = OH\cdot CH_2\cdot CO\cdot[CH\cdot OH]_3\cdot CH_2\cdot OH + H_2O$, but on more prolonged oxidation erythritic acid is formed:

$$OH\cdot CH_2\cdot CO\cdot[CH\cdot OH]_3\cdot CH_2\cdot OH + O_2 = OH\cdot CH_2\cdot COOH + OH\cdot CH_2[CH\cdot OH]_2\cdot COOH.$$

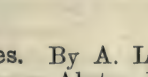
V. H. V.

Cyclamose, a New Sugar. By G. Michaud (*Chem. News*, **53**, 232).—*Cyclamose*, $C_{12}H_{22}O_{11}$, is found in the tubercles of *Cyclamen Europæum*. The tubercles are digested for a few days with 80 per cent. alcohol, the filtered solution is concentrated and mixed with large excess of 96 per cent. alcohol. The precipitated sugar is dissolved in water, mixed with lime, the solution treated with alcohol, and the precipitated lime compound washed with alcohol, dissolved in water, and decomposed by a current of carbonic anhydride. The solution of sugar is evaporated over sulphuric acid in a vacuum. Cycla-

mose is lævorotatory. Its rotatory power = − 15·15°, is not affected by temperature, is decreased by basic lead acetate; hydrochloric acid at 65° at first increases it to − 66·54 at 15°, but this number soon decreases on further heating. Cyclamose reduces Fehling's solution and can be inverted by dilute acids. D. A. L.

The Violet Coloration of Starch caused by Iodine Chloride and Bromide. By H. Beckurts and W. Freytag (*Chem. Centr.*, 1886, 454—455).—In testing potassium iodide for iodate by means of sulphuric acid and starch solution, a violet coloration is often noticed. The author finds that a similar colour is formed when chlorine or bromine water is gradually added to the blue iodide of starch solution, or when a slight excess of iodine is added to yellow bromide or chloride of starch. The coloration is undoubtedly due to the formation of a compound of starch and chloride or bromide of iodine. This colour, like the blue iodine coloration, disappears when the solution is boiled and reappears on cooling. The author believes the presence of traces of chlorate to be the cause of the violet colour appearing during the testing of potassium iodide. L. T. T.

Decomposition of Amines of the Fatty Series. By A. Muller (*Bull. Soc. Chim.*, **45**, 438—440).—Mono-, di-, and tri-methyl- and ethyl-amines, as also monobutylamine and a mixture of ammonia and ethylene, were decomposed by passing their vapours through a porcelain tube heated to a known temperature, between 1100° and 1300°; the duration of the experiment was noted, and the decomposition products, which consisted of hydrogen cyanide, ammonia, nitrogen, carbon, methane, hydrogen, ethylene, acetylene and benzene, were collected and estimated. The results from the experiments are in accordance with the theory of maximum work. A. P.

Bases from Aldoximes. By V. Meyer and A. W. Warrington (*Ber.*, **19**, 1613—1614).—When acetyl chloride acts on aldoximes or acetoximes it usually produces with the former nitriles (with the separation of water), with the latter acetyl-derivatives. Camphoroxime forms, however, an exception, giving a nitrile like an aldoxime. *Isobutyrone acetoxime*, NOH : $C(CHMe_2)_2$—a colourless oil boiling at 180°—yields an anhydride which, however, is not a nitrile, but a well-marked base. This base is an oil of intense odour, and its hydrochloride is soluble in water. The probable formula is  . L. T. T.

Tiglic Aldehyde and its Derivatives. By A. Lieben and S. Zeisel (*Monatsh. Chem.*, **7**, 53—74; compare Abstr., 1881, 710).—*Tiglic aldehyde* or *α-β-dimethylacrolein*, CHMe : CMe·CHO, is prepared by heating acetic acid (1 mol.) and propionic aldehyde (1 mol.) with an equal volume of sodium acetate solution (27·7 per cent.) in sealed tubes at 100°. It is a colourless liquid with a very pungent odour; it boils at 115·8° (corr.) at a pressure of 738·9 mm. It combines with bromine, forming a *dibromovaleraldehyde*, $C_5H_8Br_2O$, is

soluble in 40—50 parts of water, and combines with sodium hydrogen sulphite. Herzig's statement (Abstr., 1882, 593) as to its identity with guaial is confirmed.

When reduced with iron filings and acetic acid, tiglic aldehyde yields *valeraldehyde*, an amylic alcohol, boiling at 128—129°, which from a study of its derivatives was shown to be *methylethylcarbinol*, $CHMeEt{\cdot}CH_2OH$, and an unsaturated alcohol, $C_5H_{10}O$, boiling at 125—135°, which may be considered as *α-β-dimethylallylic* or *tiglylic alcohol*. On treating the mixture containing the unsaturated alcohol with bromine and distilling, converting the impure residue into triacetate and subsequently treating with baryta-water, another substance, *pentenyl glycerol*, $OH{\cdot}CHMe{\cdot}CMe(OH){\cdot}CH_2{\cdot}OH$, was obtained. It is a thick, colourless liquid boiling at 163·4—165·4° under a pressure of 30 mm. When oxidised by the action of free oxygen in the same way as methylethylacroleïn (Abstr., 1883, 570), tiglic aldehyde yields tiglic acid, acetic acid, formic acid, carbonic anhydride, and fatty acids not volatile in steam. G. H. M.

Methylpropylpinacoline. By F. Szymanski (*Ber.*, **19**, 1532—1534).—*Methylpropylpinacoline*, $C_{10}H_{20}O$, is prepared by reducing methyl propyl ketone (obtained from ethylic ethylacetoacetate) by Wislicenus's method (Abstr., 1883, 966) to the corresponding pinacone; this when boiled for several days with a mixture of sulphuric acid (1 part) and water (4 parts) yielded the pinacoline which was distilled with steam, dried with potash, and fractionated. It forms a pale yellow liquid having an odour of camphor; it is insoluble in water and boils at 182—187° (uncorr.). It does not form a compound with hydrogen sodium sulphite: this result points to the constitution $COPr{\cdot}CMe_2Pr$ rather than $COMe{\cdot}CMePr_2$ for methyl propyl pinacoline. N. H. M.

Butyl Monochloracetate. By G. Gehring (*Compt. rend.*, **102**, 1399—1401).—Butyl monochloracetate is obtained by passing dry hydrogen chloride into a solution of monochloracetic acid in an equivalent quantity of normal butyl alcohol. It is a colourless, mobile liquid with a pleasant fruity odour and a burning taste, and is slowly saponified by aqueous potash. It boils at 175°; sp. gr. at 0° = 1·103, at 15° = 1·081; vapour-density 5·1.

The boiling points of the ethereal salts of monochloracetic acid increase by about 14° for each increment of CH_2. C. H. B.

Amyl Monochloracetate. By L. Hugounenq (*Bull. Soc. Chim.*, **45**, 328—329).—Theoretical quantities of crystallised monochloracetic acid and amyl alcohol are boiled with a small quantity of concentrated sulphuric acid in a reflux apparatus, the liquid formed is poured into cold water, and the oily layer obtained washed, dried over calcium chloride, and twice fractioned. The portion boiling at 190° under 751·5 mm. pressure (corr.), which consists of *amyl monochloracetate*, is a colourless, mobile liquid having a fruity odour; it is almost insoluble in water but dissolves in alcohol in all proportions, its sp. gr. = 1·063 at 0°. A. P.

Action of Hydroxylamine on Capronitrile. By O. JACOBY (*Ber.*, **19**, 1500—1506).—*Capramidoxime*, $C_5H_{11}\cdot C(N\cdot OH)NH_2$, is prepared by digesting 10 grams of capronitrile, 8 grams of hydroxylamine hydrochloride, 2·8 grams of sodium dissolved in absolute alcohol, and sufficient absolute alcohol to form a homogeneous mixture for 30 hours at 100°; the product is then filtered and distilled in a vacuum. The residue is extracted with ether, and the oily substance obtained by evaporating the ether placed over sulphuric acid, when it mostly solidifies. It crystallises from benzene in splendid silvery plates with a fatty lustre, and melts at 58°; it is sparingly soluble in water, readily in alcohol, ether, benzene, &c., also in caustic potash and hydrochloric acid. The *hydrochloride* forms white needles readily soluble in water and alcohol; it melts at 116°, and is very hygroscopic. The *acetyl-derivative* forms very thin, white, lustrous scales melting at 87°, readily soluble in ether and alcohol, almost insoluble in water. The *benzoyl-derivative* is prepared by gradually adding benzoic chloride to capramidoxime and afterwards warming slightly. It crystallises in matted needles soluble in alcohol, ether and benzene; it melts at 105—106°. Both these compounds dissolve readily in hydrochloric acid, but are insoluble in caustic alkali. *Ethyl capramidoxime*, $C_5H_{11}\cdot C(N\cdot OEt)NH_2$, is obtained by heating capramidoxime dissolved in absolute alcohol with the theoretical amount of ethyl iodide and sodium. It forms long needles melting at 35°, and is very hygroscopic. It is readily soluble in alcohol, benzene, &c., sparingly in water *Capronyl capramidoxime*, $C_5H_{11}\cdot C(N\cdot O\cdot CO\cdot C_5H_{11})\cdot NH_2$, is formed when capramidoxime is boiled with aniline for four hours. The product is treated with benzene and filtered; on the addition of light petroleum to the filtrate, a dark brown, lustrous precipitate is formed. This is carefully sublimed. It forms a white, light, lustrous substance melting at 115°, readily soluble in alcohol, ether and benzene, and in hydrochloric acid. Hot caustic potash decomposes it with formation of caproic acid.

Carbonyl dicapramidoxime, $CO[NO\cdot C(C_5H_{11})\cdot NH_2]_2$, is prepared by adding a 20 per cent. solution of carbonyl chloride in benzene to a solution of capramidoxime in benzene. The product is filtered, the solid substance treated with warm water, which extracts the capramidoxime hydrochloride which is present, and dissolved in alcohol; on the addition of water it separates in lustrous, matted needles which melt at 114°. It is readily soluble in alcohol and chloroform, less soluble in ether, and insoluble in water and benzene. Hot caustic alkali decomposes it into capramidoxime and carbonic anhydride.

Capramidoxime chloral, $C_5H_{11}\cdot C(N\cdot OH)NH_2,CCl_3\cdot CHO$, is obtained by heating capramidoxime with an excess of chloral for a long time; the product is treated with much water and crystallised from benzene. It forms lustrous plates melting at 130°, readily soluble in alcohol, ether, chloroform, and in hot water and benzene. N. H. M.

Ethereal Hydrogen Oxalates and the Action of Phosphoric Chloride on Ethereal Oxalates. By R. ANSCHÜTZ and F. SCHÖNFELD (*Ber.*, **19**, 1442—1445). — *Propyl hydrogen oxalate*, $COOPr^{\alpha}\cdot COOH$, prepared in manner similar to the corresponding

ethyl salt (Anschütz, Abstr., 1884, 296), is a colourless liquid boiling at 118—119° under 13 mm. pressure. *Isopropyl hydrogen oxalate*, $COOPr^{\beta}\cdot COOH$, is also liquid, and boils at 111° under 13 mm. pressure. *Methyl hydrogen oxalate*, COOMe·COOH, is solid, but melts at the temperature of the hand, and boils at 108—109° under 12 mm. pressure. The corresponding amyl and butyl compounds could not be obtained by this reaction.

By the action of phosphoric chloride on normal amyl oxalate the authors expected to obtain the chloride $COCl\cdot COOC_5H_{11}$, which would then yield hydrogen amyl oxalate when treated with water; the reaction, however, takes another course.

Diamyl dichloroglycollate, $C_5H_{11}\cdot O\cdot CCl_2\cdot COOC_5H_{11}$, is prepared by the action of phosphoric chloride on amyl oxalate (equal mols.); it is a colourless liquid, boils at 151—152° under 13·5 mm. pressure, and is only very slowly decomposed by water. *Dipropyl dichloroglycollate*, $OPr^{\alpha}\cdot CCl_2\cdot COOPr^{\alpha}$, prepared in like manner, is a colourless liquid boiling at 111° under 12 mm. pressure. A. J. G.

Malonodinitrile. By L. Henry (*Compt. rend.*, **102**, 1394—1397).—*Malonodinitrile*, $CN\cdot CH_2\cdot CN$, is obtained by heating cyanacetamide with an equivalent quantity of phosphoric anhydride. It is a white crystalline solid which melts at 29—30°, and resolidifies to a dendritic, ice-like mass resembling its homologue succinodinitrile. Malonodinitrile boils at 218—219° under ordinary pressure, and seems to be polymerised by the prolonged action of heat; vapour-density 2·38. It has no smell and very little taste, dissolves in water, but is more easily soluble in alcohol and ether, and burns with a flame with a purple border. Concentrated hydrochloric acid dissolves it rapidly with development of heat and formation of ammonium chloride and malonic acid. The prolonged action of hydrochloric acid in sealed tubes at 150° yields monochloracetic acid and carbonic anhydride.

Malonodinitrile has acid properties which, however, are less marked than those of hydrocyanic acid. With ammoniacal silver nitrate it yields a white precipitate which seems to have the composition $CN\cdot CAg_2\cdot CN$; it turns yellow when exposed to light, and decomposes with a slight explosion when heated. C. H. B.

Sulphochloracetic Acid. By R. Andreasch (*Monatsh.*, **7**, 158—175).—The potassium salt of this acid was obtained by Rathke (this Journal, 1872, 391) by the action of potassium sulphite on trichloracetic acid.

Sulphochloracetic acid, $SO_3H\cdot CHCl\cdot COOH$, is best prepared by the action of chlorosulphonic acid on monochloracetic acid; after purification by conversion into the barium salt, &c., it is obtained as a hygroscopic, crystalline mass composed of concentrically grouped needles. The barium ($+ H_2O$), potassium ($+ 1\frac{1}{2}H_2O$), ammonium, lead, and silver ($+ \frac{1}{2}H_2O$) salts are described. The acid is also formed in the oxidation of thiohydantoïn by means of potassium chlorate and hydrochloric acid.

Barium dibromomethanesulphonate, $(CHBr_2\cdot SO_3)_2Ba$, is formed, to-

gether with carbonic anhydride, by the action of bromine on barium sulphoacetate; it crystallises in thin plates of fatty lustre.

By the action of bromine on barium sulphopropionate, monobarium sulphopropionate, $(C_3H_5SO_5)_2Ba$, is formed.

Barium sulphochloracetate when treated with bromine yields *barium chlorobromomethanesulphonate*, $(CHClBr{\cdot}SO_3)_2Ba$; this crystallises in thin, satiny, rhomboidal plates.

Chloromethanedisulphonic acid, $CHCl(SO_3H)_2$, is obtained as a bye-product in the preparation of sulphochloracetic acid; it forms very deliquescent needles. The barium and silver salts are described.

A. J. G.

Diphenylthiënylmethane. By L. E. Levi (*Ber.*, **19**, 1623—1625).—Adapting Hemilian's method (*Ber.*, **7**, 1203) for the preparation of triphenylmethane by acting on a mixture of benzhydrole and benzene with phosphoric anhydride, the author treated a mixture of 10 grams of benzhydrole and 5 grams of thiophen with excess of phosphoric anhydride. The reaction took place more readily than with benzene, and was completed without the aid of external heat.

Diphenylthiënylmethane, $C_4SH_3{\cdot}CHPh_2$, thus obtained, forms white scales melting at 63°, and boiling at 330—340°. It is easily soluble in acetic acid, ether, alcohol and benzene, and when slowly crystallised from the latter solvent yields short needles containing 1 mol. C_6H_6 and melting at 48°.

All attempts to obtain hydroxy-, nitro-, or amido-derivatives (and thence an analogue of rosaniline) proved unavailing. The *acetyl-derivative*, $CHPh_2{\cdot}C_4SH_2Ac$, was obtained by means of Craft's reaction, but on nitration the thiophen-group was split off, nitracetothiënone being formed.

L. T. T.

Methylthiophensulphonic Acid. By F. Muhlert (*Ber.*, **19**, 1620—1623).—Hitherto no sulphonic acids of the homologues of thiophen have been obtained. By employing Krekeler's method (this vol., p. 538) of acting on the phenone with sulphuric acid, the author has now succeeded in obtaining methylthiophensulphonic acid. 10 grams of acetomethylthiënone (Demuth, this vol., p. 228) were heated to 100°, then 15 grams of fuming sulphuric acid added, and the whole carefully warmed until the mass began to froth and give off sulphurous anhydride. The aceto-group is thus replaced by the sulphonic group, and *α-methylthiophensulphonic acid*, $C_4SH_2Me{\cdot}SO_3H$, produced. The free acid thus prepared was a thick syrup, which could not be obtained in a crystalline form and became red when exposed to the air. The *lead salt* is a white powder, and when distilled with its own weight of ammonium chloride yielded an oil showing Laubenheimer's reaction. The *potassium* $(+ \frac{1}{2}H_2O)$ and *zinc* $(+ 3\frac{1}{2}H_2O)$ *salts* form white crystals. The *chloride*, $C_4SH_2Me{\cdot}SO_2Cl$, was obtained as an oil which was still liquid at −10° but was not pure. The *amide* formed white crystals melting at 78—80°.

L. T. T.

Thiophenol and the α-Naphthol of the Thiophen Series. By A. Biedermann (*Ber.*, **19**, 1615—1620). By gradually adding

zinc thiophensulphinate (Weitz, Abstr., 1884, 1130) to a mixture of zinc and hydrochloric acid, the author succeeded in obtaining *thiënyl-hydrosulphide*, $C_4SH_3{\cdot}SH$, but the yield was very small, only about 2 per cent. This substance is a pale yellow oil of unpleasant odour, and boils at 166°. When exposed to the air, it is gradually converted into a solid crystalline mass, which is probably thiënyl disulphide, $(C_4SH_3)_2S_2$. The hydrosulphide dissolves in concentrated sulphuric acid to a yellow solution, which on the addition of a little isatin becomes violet in colour. Characteristic precipitates were obtained with an alcoholic solution of the hydrosulphide and many metallic salts. With diazo-compounds the hydrosulphide forms azo-colouring matters, thus differing in its behaviour from phenyl hydrosulphide. Staedler (Abstr., 1885, 1205) has observed a similar difference in the amides of these two series.

Fittig and Jayne (Abstr., 1885, 545) have shown that α-naphthol is formed when a solution of phenyl isocrotonic acid is boiled. By heating a mixture of β-thiophenaldehyde (this vol., p. 536), sodium succinate, and acetic acid at 135°, and dissolving the product in boiling dilute soda, the author obtained *hydroxythionaphthen*, $C_8SH_5{\cdot}OH$ [OH = 4]. This substance crystallises in long needles having an odour resembling that of phenol. It is soluble in alcohol and ether, sparingly so in water, melts at 72°, and sublimes unchanged. With diazobenzenesulphonic acid, it gives a red coloration, with diazobenzene hydrochloride a yellow crystalline precipitate, $C_6H_5{\cdot}N_2{\cdot}C_8SH_4{\cdot}OH$. It gives the indophenin reaction with sulphuric acid and isatin. Ferric chloride gives a violet precipitate, bleaching powder first a green, then a violet coloration. When an alkaline solution is heated with chloroform, it gives an intense bluish-green coloration. When heated in alcoholic solution with nitroso-dimethylaniline it gradually gives a blue coloration. This substance therefore resembles α-naphthol in its properties.

The author points out that in his previous communication (this vol., p. 536) the group $C_4SH_3{\cdot}CH_2$— was called *thiënyl*, whilst he wrote it *thenyl*, the former term being already employed for the group C_4SH_3—.

L. T. T.

Oxidation of Metabromotoluene. By W. A. Noyes and C. Walker (*Amer. Chem. J.*, **8**, 185—190).—Metabromotoluene was prepared from paracetotoluide; it is oxidised by an alkaline ferricyanide solution a little more easily than either the ortho- or para-compound.

Oxidation of Metatoluenesulphonamide.—The substance for experiment was prepared from orthotoluidine by converting into orthobromotoluene, sulphonating, and then removing the bromine by boiling with potash and zinc-dust. This method of replacing bromine by hydrogen is recommended as being much easier and quicker than the usual method, in which sodium amalgam is used. The solution being neutralised, the zinc is precipitated as hydroxide, and the sodium sulphate removed by aid of its insolubility in alcohol. The metatoluenesulphonic acid thus prepared was oxidised with potassium ferricyanide as in the preceding cases. Metasulphaminebenzoic acid melts at 246—247° (not 235°, Palmer); the di-silver salt is amorphous.

The following table shows the weight of the substituted benzoic acid obtained when 1 gram of each substance mentioned is oxidised with 25 grams of potassium ferricyanide:—

Toluene, 0·009.

Nitrotoluene, ortho-, 0·69; meta-, 0·052; para-, 0·73.

Bromtoluene, ortho-, 0·0044; meta-, 0·0115; para-, 0·0065.

Toluene sulphamide, ortho-, 0·59 +; meta-, 0·75; para-, 0·80.

H. B.

Aromatic Carbonates. By G. L. Löwenberg (*Chem. Centr.*, 1886, 390).—*Dinitrophenyl carbonate*, $CO[OC_6H_3(NO_2)_2]_2$ [O : NO_2 : NO_2 = 1 : 2 : 4], prepared by gradually dissolving phenyl carbonate in well-cooled fuming nitric acid, forms white needles melting at 127°. When this substance is heated with alcohol in sealed tubes at 120°, *dinitrophenetoïl*, $C_6H_3(NO_2)_2$·OEt, is formed. When reduced with tin and hydrochloric acid, the dinitro-salt yields *nitramidophenyl carbonate*, which forms colourless crystals subliming with decomposition at 170°. This yields a *hydrochloride*, $C_{15}H_{10}N_2O_7$,2HCl, and a *platinochloride*, and when treated with chromic mixture is converted into the *carbonate* of *mononitroxyquinone*, $CO[O{\cdot}C_6H_2(NO_2)O_2]_2$. This salt crystallises in pale-brown needles and melts at 260°. When boiled with concentrated hydrochloric acid the nitramido-salt yields the nitramidophenol $OH{\cdot}C_6H_3(NH_2){\cdot}NO_2$ [OH : NH_2 : NO_2 = 1 : 2 : 4].

When treated with bromine, phenyl carbonate yields *dibromophenyl carbonate* crystallising in silky needles and melting at 165—166°.

α-Naphthyl carbonate, $(C_{10}H_7)_2CO_3$, was prepared by heating sodium α-naphthoxide with carbonic oxychloride in closed tubes at 140—150°; it melts at 142°. *β-Naphthyl carbonate*, similarly prepared, melts at 105°. *Eugenyl carbonate*, $[C_6H_3(OMe){\cdot}C_3H_5]_2CO_3$ (obtained in the same way as the naphthol-derivatives), melts at 93°, and the compound $[C_6H_4(COH)]_2CO_3$ (from the sodium salt of salicylic aldehyde and carbonyl chloride) at 94—95°. *Phenyldithiocarbonate*, $Ph_2 : S_2 : CO$, was obtained from phosgene gas and thiophenol; it melts at 72°.

L. T. T.

Orthoisopropylphenol. By M. Fileti (*Gazzetta*, **16**, 113—131).—Three isopropylphenols have been described, one by Paternò and Spica (Abstr., 1880, 882), melting at 61° and boiling at 226°; another by Spica, boiling at 218·5° and not solidifying in a freezing mixture; and a third by the author, obtained by the action of nitrous acid on cumidine, which boils at 212°, and solidifies in a freezing mixture, the crystals melting at 8—10°. It would thus appear that the last two substances are not identical, but isomeric, and in the present paper a full description is given of the 1 : 2 isopropylphenol from the 1 : 2 cumidine. It is a colourless liquid, strongly refractive, and of phenolic odour; it melts at 15°, and boils at 212—212·5° under a pressure of 732·5 mm.; sp. gr. = 1·0124 at 0° and 0·9276 at 100° (water at 4° = 1); mean coefficient of expansion between 0° and 100° = 0·000914.

The *acetyl-derivative*, $C_6H_4Pr^{\beta}{\cdot}OAc$, is a colourless, strongly refractive liquid, boiling at 228·7°, sp. gr. = 1·0271 at 0° and 0·9382 at 100° (water at 4° = 1). It is decomposed by water after prolonged boiling.

The *methyl ether*, $C_6H_4Pr^{\beta}\cdot OMe$, is a colourless liquid, boiling at 198—199°. The *ethyl ether* is a colourless liquid, boiling at 209°; sp. gr. = 0·944 at 0° and 0·8591 at 100° (water at 4° = 1).

Monobromisopropylphenol, $C_6H_3Pr^{\beta}Br\cdot OH$ (Pr^{β} : OH : Br = 6 : 1 : 4), is prepared by the bromination of the phenol in acetic acid solution. It crystallises in white needles, melts at 47—49°, and boils at 250°; it is insoluble in water, soluble in other menstrua. It dissolves also in potash, and is reprecipitated by hydrochloric acid as a liquid. On nitration it forms a nitro-derivative melting at 33°. Its *methyl ether* is a colourless liquid boiling at 250·8°.

Dibromisopropylphenol, $C_6H_2Pr^{\beta}Br_2\cdot OH$ [Pr : OH : Br_2 = 6 : 1 : 2 : 4], obtained by bromination of the monobromo-derivative, is a colourless liquid, decomposed completely on distillation. Its *methyl ether* is a viscid liquid of ethereal odour, boiling at 278—280°.

On nitrating the phenol, two mononitro-derivatives are obtained, the one solid, non-volatile in steam, the other liquid and volatile in steam. Of these, the former only was obtained in a pure state. It crystallises in colourless needles which melt at 86°; they are soluble in the ordinary menstrua, as also in the alkalis and their carbonates. With bromine it gives a bromo-derivative, crystallising in laminæ, which melts at 88° and is volatile in steam.

Bromonitroisopropylphenol, $C_6H_2Pr\cdot Br(NO_2)\cdot OH$ [Pr : OH : NO_2 : Br = 6 : 1 : 2 : 4], obtained by nitration of the bromo-derivative, crystallises in delicate needles, which melt at 33°.

By the action of sodium and carbonic anhydride on the isopropylphenol, a mixture of the *mono-* and *di-carboxylic acids* is obtained, of which the former is soluble, the latter insoluble, in chloroform. The *monocarboxylic* acid (Pr : OH : COOH = 6 : 1 : 2) crystallises in long colourless needles, melting at 71—72°, and turning violet on exposure to light. Its *lead* salt is amorphous; its *silver* salt crystallises in white needles. The *dicarboxylic* acid crystallises in tabular or acicular crystals, melting at 295°, and is very soluble in water, ether and alcohol, insoluble in benzene and petroleum.

Isopropylphenylglycollic acid, $C_6H_4Pr\cdot O\cdot CH_2\cdot COOH$, obtained from the phenol and monochloracetic acid, crystallises in glistening needles which melt at 130—131°; its *barium* salt forms a crystalline crust, the *silver* salt white needles, the *lead* and *copper* salts amorphous precipitates.

By the action of phosphoric bromide on the phenol a *phosphoric* ether and 1 : 2 bromocumene are produced. The former is a viscid liquid, boiling at 375—380° at a pressure of 280 mm.; it is insoluble in water, soluble in ether and alcohol. V. H. V.

Preparation of Quinone and Quinol. By R. Nietzki (*Ber.*, **19**, 1467—1469).—The author's processes for the preparation of these substances (Abstr., 1878, 315 and 794) have recently been modified by Seyda (Abstr., 1883, 1115). The author points out several objectionable points in these modifications, and recommends the following procedure:—A concentrated solution of sodium dichromate (1 part of salt in 2 to 3 parts of water) is slowly added to a mixture of 1 part of aniline, 25 parts of water and 8 parts of sulphuric acid,

the liquid being well cooled; the addition of the chromate solution is continued until any quinhydrone formed has been oxidised to quinone. Instead of extracting the quinone with ether and then reducing it to quinol, it is best to reduce at once with sulphurous anhydride, filter off the insoluble impurities, and extract the quinol with ether. Operating in this way, a yield of 85 per cent. of crude quinol (on the aniline employed) has been obtained. A. J. G.

Action of Sulphuric Acid on Phthalic Alcohol. By E. Hjelt (*Ber.*, **19**, 1538—1540).—When phthalic alcohol is heated with sulphuric acid diluted with half its weight of water, a fine yellow powder is formed, insoluble in the usual solvents. It melts at a very high temperature with decomposition. Analyses of different preparations did not give concordant results, but the author considers it to be identical with a compound, $(C_8H_8O)_n$, obtained by Grimaux (*Annalen*, **155**, 343) by the action of water at 200° on xylylene bromide. It is very indifferent towards reagents.

When the reaction is allowed to take place at a temperature not much above 70°, an oil is formed; analyses point to the formula $C_{16}H_{16}O_3$. N. H. M.

Action of Potassium Cyanide on Dinitroaniline. By E. Lippmann and F. Fleissner (*Monatsh. Chem.*, **7**, 95—98).—An alcoholic solution of 2 : 4 dinitroaniline (1 mol.) is heated to 60°, and an alcoholic solution of potassium cyanide (1 mol.) added very slowly. The liquid boils, turns brownish-red with evolution of ammonia, and after being left for some time in the cold deposits a dark precipitate of the impure potassium salt of dinitramidophenol. This is purified by washing with alcohol, solution in water, and reprecipitation with hydrochloric acid; the precipitate is then dried, and the dried mass extracted with chloroform.

Dinitramidophenol crystallises from hot chloroform in brownish-red shining crystals, melts at 225°, and is readily soluble in alcohol and ether. It is reduced by hydrogen sulphide, and its salts, which are yellowish-red, detonate when heated. When boiled in aqueous alkaline solution, ammonia is given off, and *dinitroresorcinol* is formed in theoretical amount; this melts at 145°, and is identical with that described by Benedikt, showing that dinitroamidophenol has the constitution $[OH : NH_2 : (NO_2)_2 = 1 : 3 : 4 : 6]$.

Picramic acid, which is known to have the constitution

$$[OH : NH_2 : (NO_2)_2 = 1 : 2 : 4 : 6],$$

is not decomposed by boiling with alkalis, consequently it appears that here it is the position of the amido-group which is of importance. G. H. M.

Action of Aniline on Dibromosuccinic Acid. By A. Reissert (*Ber.*, **19**, 1644—1645).—Referring to Michael's recent paper (this vol., p. 698), the author has compared the anil and anilid obtained by that investigator with the compounds previously described by the

author in conjunction with Tiemann (this vol., p. 551), and finds them to be identical. It thus appears that when aniline acts on dibromosuccinic acid, hydrogen bromide is first separated, bromofumaric acid being formed, and that this latter then reacts with the aniline to form the two compounds described. The author considers Michael's formulæ to be most probably correct. L. T. T.

Fumaric and Succinic Derivatives of Monamines. By A. Piutti (*Gazzetta*, **16**, 153—161).—When secondary aromatic amines are heated with fumaric or malic acid, derivatives of *fumaramic* acid and *fumaride* are produced, the former at the lower, the latter at the higher temperature.

Diphenylfumaramic acid, $COOH\cdot CH : CH\cdot CONPh_2$, crystallises in small needles which melt at 120—121°, and are soluble in alcohol. Its alkaline salts are soluble; the copper salt is a bluish-green precipitate.

Diphenylaminefumaride has been previously described (this vol., p. 621).

Methylphenylfumaramic acid, $COOH\cdot C_2H_2\cdot CONMePh$, crystallises with $2H_2O$ in prismatic tables; it becomes anhydrous at 100°, and melts at 128°; it is insoluble in water, but soluble in alcohol and ether. Its *alkaline* salts are very soluble; its *silver* salt crystallises in aggregates of small prisms. With bromine, the acid yields a *dibromo-derivative* crystallising in shining prisms, which melt at 178°.

Methylphenylaminefumaride, $(NMePh)_2C<\overset{CH : CH}{\underset{O}{\quad}}>CO$, crystallises in glistening prisms which melt at 187·5—188°; it is readily soluble in alcohol and ether.

Methylphenylaminesuccinide, $(NMePh)_2C<\overset{CH_2\cdot CH_2}{\underset{O}{\quad}}>CO$, obtained from methylaniline and succinic acid, crystallises in small prisms which melt at 156·5°. The corresponding ethyl-derivative melts at 106°, and is decomposed by concentrated potash into succinic acid and ethylaniline. V. H. V.

Dimethylaniline-derivatives. By V. Merz and W. Weith (*Ber.*, **19**, 1570—1576).—Dimethylaniline and sulphur chloride, preferably in very dilute benzene or petroleum solution, form *dithiodimethylaniline*, $S_2(C_6H_4\cdot NMe_2)_2$, which crystallises in glistening needles, melting at 118°. It is soluble in carbon bisulphide, sparingly soluble in benzene, ether and petroleum; with acids it forms readily decomposable salts only obtained in an amorphous, gummy condition; with platinic chloride it gives a golden flocculent precipitate of the composition $S_2(C_6H_2NMe_2)_2PtCl_4$. Ammoniacal solution of silver nitrate converts it into *dioxydimethylaniline*, $O_2(C_6H_4\cdot NMe_2)_2$, which crystallises in golden needles melting at 90·5°, sparingly soluble in water, soluble in alcohol and ether. The dithio-derivative on hydrogenation with tin and hydrochloric acid is converted into a dimethylamidothiophenol, which, owing to its ready oxidisability, was not isolated as such, but its existence confirmed by preparation of the crystalline lead compound, $(NMe_2\cdot C_6H_4\cdot S)_2Pb$; but this compound in presence of acetic acid is oxidised on contact with air into dithio-

dimethylaniline. On hydrogenation with sodium amalgam, hydrogen sulphide and dimethylaniline are produced. V. H. V.

Cyanhydrin of Nitrosodipropylaniline. By A. Mandl (*Monatsh. Chem.*, **7**, 99—104).—Nitrosodipropylaniline is prepared by treating dipropylaniline (b. p. 240—242°) with hydrochloric acid and water and adding pure sodium nitrite, keeping the mixture well cooled. On addition of soda, the free base separates at first as an oily substance but soon becomes solid. Nitrosodipropylaniline so prepared is very soluble in alcohol, ether, chloroform and benzene, and must be crystallised from light petroleum. It forms chrome-green, asymmetric crystals, $a : b : c = 0{\cdot}5759 : 1 : 0{\cdot}2767$, melts at 42°, and is converted into nitrosophenol and dipropylamine when boiled with dilute alkalis. The platinochloride is obtained as a brown, crystalline precipitate which can be recrystallised from dilute hydrochloric acid.

The *cyanhydrin*, $C_{25}H_{37}N_5O_2$, is prepared by boiling together on a water-bath alcoholic solutions of nitrosodipropylaniline (1 mol.) and potassium cyanide free from alkali (1 mol.). It forms ruby-red, asymmetric crystals, $a : b : c = 0{\cdot}8068 : 1 : 1{\cdot}9993$, melts at 140°, is insoluble in water, sparingly soluble in cold alcohol and ether, easily soluble in boiling alcohol and chloroform, and soluble in hydrochloric acid with a red colour.

Treated with nascent hydrogen, the cyanhydrin splits up into ammonium formate and dipropylphenylenediamine. Formic acid was also present in the products of the action. From this there can be no doubt that the cyanhydrin has the composition

$$\begin{matrix} C_6H_4{\cdot}NPr_2{\cdot}NO \\ \quad\quad\quad\

in leaflets, and the *acetyl-derivative* in hard crystals, melting at 65°. On reduction it is converted into the corresponding amidine, which forms leaflets, melting at 79°, soluble in alcohol, ether and chloroform.

Benzylenimide, $C_6H_4<\begin{matrix}NH\\CH_2\end{matrix}>$, obtained as a reduction product of nitrobenzylic chloride, is a yellowish-grey, soluble powder; its salts form dark red solutions, but are not readily obtained in a state of purity; its *platinochloride* is an insoluble, amorphous red powder.

V. H. V.

Nitro- and Bromo-derivatives of Azobenzene. By J. V. Janovsky (*Monatsh.*, **7**, 124—138).—The melting point of the more soluble trinitro-azobenzene obtained by the action of nitric acid on diparanitro-azobenzene is 160° (uncorr.), not 169° as previously stated (Abstr., 1885, 894).

Paranitro-azobenzene when nitrated yields, not as previously stated one, but two trinitro-derivatives. The compound more soluble in alcohol crystallises in microscopic, ochre-yellow, rhombic needles, and is probably identical with that obtained by Petrieff by the direct nitration of azobenzene. On reduction it yields paraphenylenediamine, and a triamidobenzene, which could not be obtained in a state sufficiently pure for further examination. The second compound, $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(NO_2)_2$ [3 : 3 : 4], crystallises in brilliant rhombic tables, showing the combinations $\breve{P}\infty$, $\infty\breve{P}\infty$ or P, ∞P, $\infty\breve{P}\infty$. Its constitution is proved by its formation from both paranitro-azobenzene and dimetanitroazobenzene.

Dimetanitro-azobenzene when nitrated yields, in addition to that just mentioned, another trinitro-compound more soluble in alcohol and acetone; this crystallises in lustrous, clear yellow prisms, melts at 126·8° (corr.), and gives an emerald-green coloration with ammonium sulphide and alkalis.

Orthonitro-azobenzene, $C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}NO_2$ [$NO_2 = 2$], is obtained by the nitration of azobenzene dissolved in acetic acid. It crystallises in orange-red needles, melts at 129·9° (corr.), and gives with ammonium sulphide and alkalis a green coloration turning brownish-red after some time. By moderated reduction it gives an amidoazobenzene, whose colour is less intense than that of the para-compound; the hydrochloride crystallises in ruby-red prisms with blue metallic lustre. By complete reduction with tin and hydrochloric acid it yields aniline and orthophenylenediamine.

2 : 4 *Dinitro-azobenzene*, prepared by the nitration of orthonitroazobenzene, crystallises in orange-red plates, melts at 214° (corr.), and with ammonium sulphide in alkaline solution gives a blue coloration which does not change.

4 : 3 ? *Dinitro-azobenzene* is obtained in the nitration of the paranitrosulphonic acid; it crystallises in orange-red plates, melts at 211° (corr.), and also gives a permanent blue coloration with ammonium sulphide in alkaline solution.

A third new *dinitro-azobenzene* of unknown constitution is obtained by nitrating azobenzene with the aid of heat. It forms yellow, asbestos-like crystals, melts at 185° (corr.), and with ammonium

sulphide in alkaline solution gives a blue solution which rapidly turns brown.

Bromazobenzene, $C_{12}H_9BrN_2$, is obtained by the action of bromine on azobenzene (equal parts); the reaction takes about eight days for completion at the ordinary temperature, or can be effected more quickly at 100°; in the latter case the action must be conducted uninterruptedly, as a bromhydrazobenzene results from a long-continued action. Bromazobenzene crystallises in flat, lustrous, golden-yellow, rhombic needles, and melts at 85° (uncorr.). It is accompanied by a less soluble modification, which crystallises in yellow plates resembling those of lead iodide and melts at 187°. A. J. G.

Orthamidoazo- and Hydrazimido-compounds. By T. Zincke and A. T. Lawson (*Ber.*, **19**, 1452—1461). When orthoamidoazotoluene dissolved in a little alcohol and mixed with excess of an acid, is treated with nitrous acid, diazoazo-salts are formed. *Orthodiazoazotoluene sulphate* crystallises in red, interlaced needles; the nitrate crystallises in needles and explodes when heated. The *chloride*, $C_{14}H_{13}N_4Cl$, crystallises in red granules, and gives a precipitate of yellow needles when treated with platinic chloride.

Diazoazotoluene perbromide, $C_{14}H_{13}N_4Br_3$, prepared by adding excess of bromine to either of the salts, crystallises in long, deep red, dichroic needles of golden lustre, and melts at 125°. When treated in the cold with alcoholic ammonia it is converted into the *imide*, $C_{14}H_{13}N_5$; this crystallises in thick, opaque, yellowish-red forms, melts at 85°, and when heated at a higher temperature decomposes explosively into nitrogen and the compound $C_{14}H_{13}N_2$, obtained by oxidising orthamidoazotoluene (Zincke, this vol., p. 236). A similar decomposition ensues when the imide is boiled with glacial acetic acid.

When the diazo-salts above described are treated with sulphurous anhydride, sulphites, or, best, stannous chloride, a reduction product, $C_{14}H_{14}N_4$, is formed. It crystallises in long, colourless, or pale yellow needles, melts at 168°, and is insoluble in water, sparingly soluble in ether and chloroform, more readily in benzene and acetic acid, readily soluble in alcohol. It does not show basic properties, yields an acetyl-derivative, $C_{14}H_{13}AcN_4$, crystallising in white plates and melting at 132—134°, does not yield definite products with benzaldehyde, amyl nitrite, ethyl chlorocarbonate, or methyl iodide, is not affected by reducing agents, and yields the perbromide above described when treated with bromine. When oxidised in alcoholic solution with silver oxide, it yields *metaparazotoluene*, $C_7H_7{\cdot}N_2{\cdot}C_7H_7$. This crystallises in reddish-brown plates, melts at 56—58°, and dissolves readily in the ordinary solvents; it is also formed by the action of zinc-dust in presence of alcohol on the diazo-salts.

The remainder of the paper is given up to a discussion of the probable constitution of these substances. A. J. G.

Action of Halogenated Amines on Phenyl Carbamide. By L. Gattermann (*Ber.*, **19**, 1639—1640).—In the hope of obtaining the chlorinated carbamide, $NPhCl{\cdot}CO{\cdot}NMeCl$ or $NPhMe{\cdot}CO{\cdot}NCl_2$, the

author allowed a mixture of dichloromethylamine and phenylisocyanate to remain for some time at the ordinary temperature. Silky needles were obtained which melted at 205—206°, and had the expected composition $C_8H_8N_2OCl_2$. The properties of this compound were, however, hardly those of a substance having either of the above formulæ, and when saponified it was found to give a chlorinated aniline. It is thus clear that there must have been a migration of one or both of the chlorine-atoms. A similar reaction appears to take place when bromacetamide acts on phenyl cyanate, the compound formed melting at 221—222°. The author is further investigating this reaction.

Chlorodiethylamine forms an oil boiling at 95°, and having a very irritating odour. L. T. T.

Benzyl-derivatives of Hydroxylamine. By F. Walder (*Ber.*, **19**, 1626—1633).—Schramm has described (Abstr., 1884, 51) dibenzylhydroxylamine, $N(CH_2Ph)_2{\cdot}OH$, and its hydrochloride, the latter crystallising in lustrous scales. The *platinochloride* forms small brownish-red crystals, sparingly soluble in water. When the base is treated with acetic chloride (care being taken to avoid an excess of the latter), *acetyldibenzylhydroxylamine*, $N(CH_2Ph)_2{\cdot}OAc$, is formed. This yields white, feathery crystals melting at 173°. It is sparingly soluble in water, easily so in alcohol. If an excess of acetic chloride is employed, benzaldehyde, benzyl benzoate and benzylamine are formed; thus the acetic chloride when in excess appears only to act as a decomposing agent. A boiling solution of hydrochloric acid in glacial acetic acid causes the same decomposition. The reaction is $N(CH_2Ph)_2{\cdot}OH = CH_2Ph{\cdot}NH_2 + C_6H_5{\cdot}COH$. Benzoic chloride, both in equal molecular proportions and in excess, yields with the base only benzyl benzoate and dibenzylhydroxylamine hydrochloride. With sodium and methyl iodide the base yields no methylated hydroxylamine, but *tribenzylbenzoxyammonium iodide*, $C_7H_7{\cdot}O{\cdot}N(C_7H_7)_3I$, is formed. This compound forms white needles sparingly soluble in water, insoluble in ether, and melts at 148°. It is of interest as being the first ammonium-derivative obtained from hydroxylamine and the first tetrabenzylised ammonium known. It is probably formed by the double decomposition of the methyl iodide with a part of the benzyl of the hydroxylamine and the reaction of the benzyl iodide thus formed on the remaining hydroxylamine, according to the equation $N(C_7H_7)_2{\cdot}OH + 2C_7H_7I = HI + C_7H_7{\cdot}O{\cdot}N(C_7H_7)_3I$. This compound is not decomposed by potash, but yields a strong, alkaline base when treated with moist silver oxide.

When dibenzylhydroxylamine in alcoholic solution is digested with an excess of benzyl chloride, *tribenzylhydroxylamine*, $N(C_7H_7)_2{\cdot}O{\cdot}C_7H_7$, is formed. This crystallises in short, white prisms, is easily soluble in alcohol and ether, insoluble in water, and melts at 119°. The *hydrochloride* forms white crystals which are sparingly soluble in water, insoluble in ether, and melt at 171—172°. The *platinochloride* forms small, orange crystals melting at 150°.

When dibenzylhydroxylamine is treated with phosphorous chloride, *benzylbenzenylamine*, $C_7H_7{\cdot}N : CHPh$, is formed. This forms a pale

yellow oil distilling at 300°, and having a strong odour resembling that of ammonia. It is insoluble in water, easily soluble in alcohol and ether. Its *hydrochloride* crystallises in scales and tables and melts at 251°. In this reaction it is probable that the expected compound, $N(C_7H_7)_2{\cdot}Cl$, is first formed, and that this changes into the hydrochloride of the tertiary amine. The base forms a crystalline additive product with methyl iodide. L. T. T.

Amidoximes and Azoximes. By F. Tiemann and A. Fock (*Ber.*, **19**, 1475—1480).—Benzenylamidoxime, $NH_2{\cdot}CPh{:}N{\cdot}OH$, forms monoclinic prisms; $a:b:c = 2{\cdot}5023:1:1{\cdot}0774$; $\beta = 89°\ 36'$. Benzenylamidoxime benzyl ether, $NH_2{\cdot}CPh{:}NO{\cdot}CH_2Ph$, also crystallises in monoclinic prisms; $a:b:c = 0{\cdot}8546:1:0{\cdot}2620$; $\beta = 82°\ 19'$. N. H. M.

Products from Benzenylamidoxime. By E. Falck (*Ber.*, **19**, 1481—1487).—The compound, $C_8H_6N_2O_2$, obtained by the action of potash on ethyl benzenylamidoxime carbonate (Abstr., 1885, 1216), is found not to contain a hydroxyl-group; the constitution $CPh\lessgtr^{N{\cdot}O}_{NH}>CO$ and the name *benzenylimidoximecarbonyl* are now ascribed to it. *Benzenylethylimidoximecarbonyl*, $CPh\lessgtr^{N{\cdot}O}_{NEt}>CO$, is obtained by heating the dry silver salt, $C_8H_5N_2O_2Ag$, of benzenylimidoximecarbonyl with ethyl iodide at 100°; it forms white needles melting at 35—36°, soluble in alcohol, ether, and benzene.

Ethylenedibenzenylamidoxime, $C_2H_4(O{\cdot}N{:}CPh{\cdot}NH_2)_2$, is formed when an alcoholic solution of benzenylamidoxime (2 mols.), sodium ethoxide (2 mols.), and ethylene bromide (1 mol.) is heated for some hours on a water-bath. It crystallises in plates soluble in alcohol, ether, benzene, &c., and readily soluble in hydrochloric acid; it melts at 155—156°. The *platinochloride* forms microscopic, yellow needles.

Chloral benzenylamidoxime, $C_9H_9N_2Cl_3O_2$, separates as a white, crystalline powder when a solution of benzenylamidoxime in the smallest quantity of chloral is treated with water. It melts at 135°, is readily soluble in alcohol and ether, insoluble in water. Sulphuric acid on prolonged heating with water decomposes it into its constituents.

Benzenyluramidoxime, $OH{\cdot}N{:}CPh{\cdot}NH{\cdot}CO{\cdot}NH_2$, is prepared by the action of benzenylamidoxime hydrochloride on potassium cyanate, both in concentrated aqueous solution. It crystallises in long, thin white needles, sparingly soluble in water, readily in alcohol, ether, and benzene, &c.; it melts at 115°. It is very indifferent in its chemical behaviour. N. H. M.

Parahomobenzenylamidoxime and its Derivatives. By L. H. Schubart (*Ber.*, **19**, 1487—1490).—*Parahomobenzenylamidoxime*. $C_6H_4Me{\cdot}C(N{\cdot}OH){\cdot}NH_2$, is obtained by heating a mixture of paramethylbenzonitrile (prepared from paratoluidine by Sandmeyer's method), hydroxylamine hydrochloride, and sodium carbonate with alcohol, and heating the clear solution for six hours at 80—90°. It crystallises

from boiling water in white plates which melt at 145—146°. It is soluble in alcohol, ether, and chloroform, &c., and is dissolved equally readily by acids and alkalis. The *hydrochloride* forms prisms melting at 186—187°. The *sodium salt*, $C_8H_9NaN_2O$, is very hygroscopic, and decomposes in moist air into parahomobenzenylamidoxime and sodium hydroxide. The *methyl salt* is prepared by boiling an alcoholic solution of the sodium salt with methyl chloride; it crystallises from water in needles which melt at 85°; the *ethyl salt* melts at 64°.

Benzoylparahomobenzenylamidoxime, $C_6H_4Me{\cdot}C(NO{\cdot}COPh)NH_2$, is prepared by adding benzoic chloride to parahomobezenylamidoxime sufficiently slowly to avoid a rise of temperature; after 24 hours the whole is washed with ammonia, and dissolved in alcohol. By careful addition of water it is precipitated in a crystalline state. It melts at 173°. When heated above its melting point it gives off water and yields *parahomobenzenylazoximebenzenyl*, $C_6H_4Me{\cdot}C\begin{smallmatrix}N{\cdot}O\\ \diagup\!\diagdown\\ N\end{smallmatrix}CPh$. The latter forms long, slender needles which melt at 103°; it is readily soluble in ether, benzene and chloroform, sparingly in hot water. It distils with steam or alone without decomposition. N. H. M.

Phenylallenylamidoxime. By H. Wolff (*Ber.*, **19**, 1507—1511). —*Phenylallenylamidoxime*, $CHPh:CH{\cdot}C(NH_2):N{\cdot}OH$, is obtained by digesting cinnamic nitrile, hydroxylamine, and sodium carbonate dissolved in dilute alcohol for several days at 60—70°; the product is evaporated in a vacuum, treated with hydrochloric acid, and extracted with ether. The aqueous solution is neutralised with sodium carbonate, and the phenylallenylamidoxime which separates, dissolved in caustic alkali, filtered, and precipitated with carbonic anhydride. It is then dissolved in dilute alcohol and decolorised by means of animal charcoal. It crystallises in prisms melting at 93°, is soluble in hot water, very readily soluble in alcohol, ether, benzene, &c. The *hydrochloride* forms flat prisms which melt at 155° with decomposition. The *platinochloride* crystallises in needles. The *benzoyl-derivative*, $CHPh:CH{\cdot}C(NH_2)NO{\cdot}Bz$, is prepared by adding a solution of benzoic chloride in absolute ether to a solution of the amidoxime in ether. It crystallises in slender needles, readily soluble in alcohol, less soluble in benzene and chloroform and insoluble in cold water. It melts at 160°.

Phenylallenylazoximebenzenyl, $CHPh:CH{\cdot}C\begin{smallmatrix}N{\cdot}O\\ \diagup\!\diagdown\\ N\end{smallmatrix}CPh$, is formed when the above benzyl-compound is boiled with water, or when it is heated above its melting point. It forms very slender, white needles readily soluble in alcohol, ether and chloroform, very readily in benzene. It melts at 102°. It is not dissolved either by acids or alkalis.

Phenylallenylazoximethenyl, $CHPh:CH{\cdot}C\begin{smallmatrix}N{\cdot}O\\ \diagup\!\diagdown\\ N\end{smallmatrix}CMe$, is prepared by heating equivalent amounts of acetic anhydride and phenylallenylamidoxime for a short time in a dish. The product is treated with acid and alkali, decolorised by means of animal charcoal, and distilled with steam. It resembles phenylallenylazoximbenzenyl

in its solubility; it melts at 78°, and sublimes when carefully heated without decomposition; the vapour has the odour of apricot.

Methyl phenylallenylamidoxime, $CHPh:CH{\cdot}C(NH_2):N{\cdot}OMe$, is prepared by the action of methyl iodide dissolved in alcohol on the sodium salt of the amidoxime. It melts at 98°, and dissolves readily in ether, alcohol, benzene and chloroform; it has only basic properties. The *ethyl salt* is obtained in a manner similar to the methyl salt, which it resembles in its solubility, &c. It melts at 83°.

Phenylallenylazoximepropenylcarboxylic acid,

$$CHPh:CH{\cdot}C\begin{matrix}N{\cdot}O\\ \diagup\!\diagdown\\ N\end{matrix}C{\cdot}CH_2{\cdot}CH_2{\cdot}COOH,$$

is prepared by melting together equivalent amounts of succinic anhydride and phenylallenylamidoxime. The product is dissolved in dilute caustic soda, filtered, diluted with water, and precipitated with hydrochloric acid. It is then dissolved in alcohol and decolorised with animal charcoal. It forms long, lustrous prisms, readily soluble in alcohol and chloroform, less soluble in ether, benzene and hot water. It melts at 114°. It is a much feebler acid than that derived from benzenylamidoxime. The *alkali salts* are readily soluble in water. The *silver salt* forms a white powder; it is rather soluble in hot water but is partly decomposed when dissolved. N. H. M.

Action of Hydroxylamine on Cinnamaldehyde Hydrocyanide. By E. Bornemann (*Ber.*, **19**, 1512—1514). *Cinnamaldoxime*, $CHPh:CH{\cdot}CH:N{\cdot}OH$, is prepared by digesting cinnamaldehyde hydrocyanide (Abstr., 1884, 1344) with free hydroxylamine for 12 hours at 30—56°. It forms very slender, lustrous needles, readily soluble in ether, chloroform, alcohol, caustic alkalis and acids, almost insoluble in cold water and light petroleum. It melts at 134—136°. It reduces Fehling's solution when warmed. The *benzoyl-derivative*, $CHPh:CH{\cdot}CH:NOBz$, crystallises in well-formed, white needles, melting at 123—125°, sparingly soluble in cold alcohol and benzene, insoluble in light petroleum. *Phenylvinylhydroxyethenylamidoxime*, $CHPh:CH{\cdot}CH(OH){\cdot}C(N{\cdot}OH){\cdot}NH_2$, is formed together with the above compound, when hydroxylamine and cinnamaldehyde hydrochloride are digested at 7°. The product of the reaction is evaporated in a warm place, extracted with ether, and dissolved in alcohol. Water is then added to the alcoholic solution which after some time yields heavy, white plates. When heated it begins to decompose at 136°, and melts at 141° to a black oily mass. N. H. M.

Product of the Reduction of Metanitro-α-methylcinnamaldehyde. By W. v. Miller and F. Kinkelin (*Ber.*, **19**, 1520—1521; compare this vol., p. 701).—The formation of a furfurane-derivative from ethyl phenoxyacetoacetate (Hantzsch, this vol., p. 707) points to a different interpretation of the result obtained by the reduction of metanitromethylcinnamaldehyde, than that previously given (*loc. cit.*): the nitro-compound could be reduced to amidohydrocinnamaldehyde, and this would yield, with elimination of water, the compound

$NH_2 \cdot C_6H_3 < \begin{matrix} CH \\ CH_2 \end{matrix} > CMe$. This constitution would account for the formation of a bromine additive compound, and for the fact that the substance when oxidised is completely destroyed. N. H. M.

Derivatives of Acetophenone, Benzylidenacetone, and Benzil. By O. Jacoby (*Ber.*, **19**, 1514—1520).—*α-Phenyl-α-anilidopropionitrile*, $CN \cdot CPhMe \cdot NHPh$, is prepared by digesting an ethereal solution of a mixture of acetophenone and acetophenonehydrocyanide with aniline for several hours at 40—50°. On cooling, large prisms separate; these are separated from the mother-liquor and crystallised from alcohol. It is a white substance, insoluble in water, sparingly soluble in alcohol, benzene and light petroleum, readily soluble in ether; it melts at 152°. When digested with hydroxylamine, it decomposes into Janny's phenylmethylketoxime (Abstr., 1883, 580), aniline, and hydrocyanic acid. *α-Phenyl-α-anilidopropionamide*, $CONH_2 \cdot CMePh \cdot NHPh$, is obtained by shaking the finely powdered anilidonitrile with sulphuric acid until it is all dissolved; it is then heated for some hours on a water-bath, poured into cooled water, and neutralised with ammonia. The yellowish-brown mass is crystallised from alcohol. It is a white substance, insoluble in water, soluble in alcohol, ether and benzene, and melts at 119°.

When a solution of α-phenyl-α-anilidopropionitrile in absolute alcohol is saturated with hydrochloric acid, symmetrical triphenylbenzene, aniline hydrochloride, and ammonium chloride are formed.

Cinnamylmethylketoxime, $CHPh : CH \cdot CMe : N \cdot OH$, crystallises in white, lustrous needles which melt at 110°; it is sparingly soluble in cold water and alcohol, readily in ether.

When benzilhydroxyamide is treated with aniline, or with hydroxylamine, it is decomposed into benzil and hydrocyanic acid.

N. H. M.

Chlorination of Acetophenone. By H. Gautier (*Compt. rend.*, **102**, 1248—1250).—The products of the action of chlorine on acetophenone cannot be separated completely by fractionation. A considerable proportion of the monochloro-derivative crystallises out, but the liquid is a mixture of the bi- and tri-derivatives containing some of the mono-derivative in solution. The liquid portion boiling at 243—250° contained 39·87 per cent. of chlorine, but was separated into two fractions, the first of which boiled at 243—247°, and the second at 247—250°. This last fraction contained 45·43 per cent. of chlorine, whilst the number calculated for the trichloro-derivative is 47·65 per cent. It is evident that, contrary to the statement of Dyckerhoff, trichloracetophenone is one of the products of the direct action of chlorine on acetophenone, and the author was also unable to confirm Dyckerhoff's statement that the prolonged action of chlorine results in the formation of benzoic chloride. He obtained evidence of the existence of a higher chloro-derivative which has not yet been isolated in a state of purity.

C. H. B

Sulphone-ketones. By R. Otto (*Ber.*, **19**, 1641—1644).—When well dried silver phenylsulphoneacetate, $SO_2Ph{\cdot}CH_2{\cdot}COOAg$, is heated, the reaction which takes place is a complicated one, but the principal product is methylphenylsulphone, and not, as the author expected, a sulphoneacetone, $CO(CH_2{\cdot}SO_2{\cdot}Ph)_2$.

When monochloracetone is allowed to act on sodium benzenesulphinate, *monophenylsulphoneacetone*, $COMe{\cdot}CH_2{\cdot}SO_2Ph$, is formed. It crystallises from alcohol in glistening scales which melt at 57—58°. When this compound is brominated, and the resulting derivative, $CH_2Br{\cdot}CO{\cdot}CH_2{\cdot}SO_2Ph$, treated with another molecular proportion of sodium benzenesulphinate, *diphenylsulphonedimethylacetone*, $CO(CH_2{\cdot}SO_2Ph)_2$, is produced. This forms hard, glassy crystals melting at 149—150°. It is sparingly soluble in alcohol, ether, and benzene, easily in boiling glacial acetic acid. This class of sulphone-ketones is being investigated by W. Otto. L. T. T.

Action of Hydrogen Peroxide on Benzoic Acid. By Hanriot (*Comp. rend.*, **102**, 1250—1251).—When benzoic acid is dissolved in 5—10 times its weight of sulphuric acid and gradually mixed with 3 times its weight of a 200 vol. solution of hydrogen peroxide also dissolved in sulphuric acid, an energetic reaction takes place. When the product is diluted with water and distilled in a current of steam, unaltered benzoic acid first passes over, and then a mixture of benzoic and salicylic acids. These two acids are separated by neutralising with barium carbonate, filtering, and boiling the filtrate with an excess of baryta solution, when the salicylic acid is precipitated in the form of a basic barium salicylate. A small quantity of another acid is produced, which is more soluble in water than salicylic acid, gives a wine-red coloration with ferric chloride, is turned brown by alkalis and even by ammonium carbonate in presence of air, and dissolves in concentrated sulphuric acid, forming a red solution.

When weaker hydrogen peroxide solution acts on a sulphuric acid solution of benzoic acid at 200°, the liquid contains a certain quantity of phenol, but no salicylic acid. It would seem, therefore, that at a high temperature parahydroxybenzoic acid is produced, but it is also possible that the phenol is a product of the alteration of salicylic acid at the high temperature. C. H. B.

Derivatives of Terephthalic Acid. By F. Ahrens (*Ber.*, **19**, 1634—1639).—In attempting to convert amidoterephthalic acid into the corresponding tricarboxylic acid by Sandmeyer's method, it was found that the basicity both of the amido-acid and of its methyl salt was so feeble that they could not be diazotised in dilute solutions. The acid was therefore diazotised in the usual way by passing nitrous anhydride through a paste of the acid moistened with strong hydrochloric acid, and the resulting mass then gradually added to the boiling copper cyanide solution. The cyano-acid formed was easily soluble in water, and could not be obtained in a pure state. It was, therefore, at once saponified with potash, when trimellitic and isophthalic acids were formed.

The author has prepared the following derivatives of terephthalic acid:—*Methyl nitroterephthalate* crystallises in prisms melting at 70°. *Methyl amidoterephthalate* melts at 126°; its crystals show the blue fluorescence found by de la Rue and Müller to be characteristic of amidoterephthalic derivatives. The *hydrochloride* of this ether forms white needles, easily decomposed by water; the *platinochloride* is crystalline. *Chlorophthalic acid* prepared by Sandmeyer's reaction from the amido-acid, is soluble in alcohol and ether, sparingly so in boiling water and melts above 300°. The *methyl salt* forms silky scales soluble in alcohol and ether, sparingly in water, and melts at 60°. The *ethyl salt* is an oil. The *chloride*, $C_6H_3Cl(COCl)_2$, boils at 300°. The *amide* forms white crystals, soluble in water and alcohol, and melts above 300°. L. T. T.

Synthesis of Orcinol from Ethyl Acetonedicarboxylate. By H. Cornelius and H. v. Pechmann (*Ber.*, **19**, 1446—1451).—*Ethyl dihydroxyphenylacetocarboxylate*, $COOEt{\cdot}CH_2{\cdot}C_6H(OH)_2(COOEt)_2$ [$CH_2{\cdot}COOEt : (OH)_2 : (COOEt)_2 = 1 : 3 : 5 : ? : ?$], is prepared by gradually adding 21 grams of finely divided sodium to 100 grams of pure ethyl acetonedicarboxylate, the mixture being at first cooled with ice water, but the operation afterwards conducted at the ordinary temperature, and finally at 120°. When all action has ceased, the product is heated quickly to 145°, cooled to 80°, boiled on the water-bath with 500 c.c. of alcohol, and the solution decomposed with dilute sulphuric acid. It crystallises in snow-white, interlaced needles, melts at 98°, can be sublimed at a higher temperature, although the greater part is then carbonised, and is sparingly soluble in alcohol, ether, and light petroleum, nearly insoluble in water, and readily soluble in alkalis. The free acid could not be obtained, as on treatment with alkalis, carbonic anhydride is eliminated and dihydroxyphenylacetic acid formed.

Dihydroxyphenylacetic acid, $C_6H_3(OH)_2{\cdot}CH_2{\cdot}COOH$, [$(OH)_2 = 3 : 5$], crystallises with 1 mol. H_2O in rhombic (?) tables or needles, is readily soluble in water, alcohol and ether, insoluble in chloroform. When exposed in alkaline solution to the air, it gives a similar red coloration to that given by orcinol, which it closely resembles in many reactions; it reduces Fehling's solution and ammoniacal silver solutions, shows the homofluorescein reaction when heated with chloroform and dilute soda, and gives a violet coloration with ferric chloride. The lead and silver salts are described. When the silver salt is heated in a current of carbonic anhydride, orcinol is obtained. A. J. G.

Carboxylic Acids of Benzenylamidoxime and its Azoxime-derivatives. By G. Müller (*Ber.*, **19**, 1491—1500; compare Abst., 1885, 1227).—Benzenylamidoximecarboxylic acid (*loc. cit.*) can be obtained by the action of free hydroxylamine on paracyanobenzoic acid.

Benzenylazoximethenylparacarboxylic acid,

$$COOH{\cdot}C_6H_4{\cdot}C\begin{matrix}<\\ \\ \end{matrix}\begin{matrix}N{\cdot}O\\ \diagup\!\diagdown\\ N\end{matrix}\begin{matrix}>\\ \\ \end{matrix}CMe\ [1 : 4],$$

is prepared by boiling benzenylamidoximeparacarboxylic acid with acetic anhydride for one hour. It melts at 218°, is soluble in hot water, less soluble in ether and chloroform. The *paracarboxylic acid* of benzenylazoximebenzenyl was prepared in manner similar to the above compound, but could not be obtained in the pure state.

Parabenzenylazoximepropenyldicarboxylic acid,

$$COOH\cdot C_6H_4\cdot C\begin{matrix}N\cdot O\\ \diagdown\!\!\diagup\\ N\end{matrix}C\cdot C_2H_4\cdot COOH,$$

is obtained by heating benzenylamidoximeparacarboxylic acid with an excess of succinic anhydride. It is soluble in alcohol, almost insoluble in ether and insoluble in benzene and chloroform; it does not melt.

Ethyl metacyanobenzoate, $CN\cdot C_6H_4\cdot COOEt$, prepared by Sandmeyer's reaction, forms slender, matted needles, melting at 48°, soluble in alcohol, ether, and benzene. When heated with hydroxylamine hydrochloride (1 mol.) and sodium carbonate ($\frac{1}{2}$ mol.) in dilute alcoholic solution at 80—100°, *ethyl benzenylamidoximemetacarboxylate*, $C_{10}H_{12}N_2O_3$, is formed; this crystallises in needles, readily soluble in alcohol, ether, and benzene, &c.; it melts at 118°. The *free acid* melts at 200°; it is soluble in hot water and alcohol, insoluble in benzene and chloroform. When the free acid is heated with a little acetic anhydride, it is converted into *benzenylazoximethenylmetacarboxylic acid*, $C_{10}H_8N_2O_3$. This melts at 217°, and is very sparingly soluble in water and benzene, more readily in alcohol, ether and chloroform.

Metabenzenylazoximepropenyldicarboxylic acid, $C_{12}H_{10}N_2O_5$, is prepared by fusing together equal molecular weights of benzenylamidoximemetacarboxylic acid and succinic anhydride; it crystallises from hot water in needles which melt at 213°. It is readily soluble in alcohol and ether, sparingly in chloroform.

Benzenylazoximebenzenylmetacarboxylic acid,

$$COOH\cdot C_6H_4\cdot C\begin{matrix}N\cdot O\\ \diagdown\!\!\diagup\\ N\end{matrix}CPh,$$

forms a crystalline powder. It melts at 218°, is soluble in glacial acetic acid, alcohol and ether, insoluble in water, benzene and chloroform.

Ethyl orthocyanobenzoate crystallises in needles, readily soluble in alcohol, ether, and benzene, &c.; it melts at 70°. When heated with free hydroxylamine for several days at 80—100° it is converted into *phthalimidoxime*, $C_6H_4\begin{matrix}C(N\cdot OH)\\ \diagdown\!\!\diagup\\ CO\end{matrix}NH$. This crystallises from dilute alcohol in white needles, melting at 250°; when boiled with ferric chloride and hydrochloric acid it yields phthalimide. N. H. M.

Paranitrobenzoicsulphinide. By W. A. Noyes (*Amer. Chem. J.*, **8**, 167—175).—Nitrotoluenesulphonamide was prepared from paranitrotoluene by the usual methods; it forms white crystals melting at 186—187°. It was oxidised in slightly alkaline and dilute aqueous solution; the filtered product of the reaction was acidified, filtered from unaltered amide and concentrated, when *potassium anhydronitro-*

sulphaminebenzoate, $NO_2 \cdot C_6H_3 < \begin{matrix} CO \\ SO_2 \end{matrix} > NK$, separated out; this salt requires 100 parts of cold water for solution. The hot aqueous solution of the potassium salt when acidified deposits *paranitrobenzoicsulphinide*, $NO_2 \cdot C_6H_3 < \begin{matrix} CO \\ SO_2 \end{matrix} > NH$ [CO : SO_2 : NO_2 = 1 : 2 : 4], melting at 209°; it is intensely bitter, as are also its salts. The barium and silver salts are described.

Para-amidobenzoicsulphinide, $NH_2 \cdot C_6H_3 < \begin{matrix} CO \\ SO_2 \end{matrix} > NH$, is obtained from the preceding compound by reduction with ammonia and sulphuretted hydrogen; it is almost insoluble in cold water, more soluble in alcohol and ether; its solution shows a dark blue fluorescence; the colourless crystals melt with decomposition at 283—285°. The potassium, barium, and silver salts are described. H. B.

Oxidation of Benzene-derivatives with Potassium Ferricyanide. By W. A. Noyes (*Amer. Chem. J.*, **8**, 176—185).—It has been supposed that the orthosulphaminebenzoic acids were not capable of separate existence, only their anhydrides being known. But by employing potassium ferricyanide instead of potassium permanganate as the oxidising agent for orthotoluenesulphonamide it is shown that the free acid may be obtained. For the preparation of orthotoluenesulphonamide, Claesson and Wallin's method—treatment of toluene with chlorosulphonic acid—was found to give the best results. At the same time an amide melting at 108—110° is formed; it is a mixture of the ortho- and para-amides.

Orthosulphaminebenzoic acid, $COOH \cdot C_6H_4 \cdot SO_2NH_2$, was prepared by boiling the orthotoluenesulphonamide with a strong, alkaline solution of potassium ferricyanide, orthobenzoicsulphinide and sulphobenzoic acid are also formed but in comparatively small quantity; after removing most of the ferrocyanide by crystallisation and unoxidised material and potassium sulphate by partial neutralisation, the product of the reaction was extracted by ether in acid solution; the barium salt was prepared, purified, and finally decomposed by hydrochloric acid. The acid crystallises well, is readily soluble in water, and has an acid but not sweet taste; its melting point varies (153—167°), owing to its gradual change into the anhydride. Two barium salts with 9 and 2 mols. H_2O respectively are described, and two silver salts $COOAg \cdot C_6H_4 \cdot SO_2NH_2$ and $COOAg \cdot C_6H_4 \cdot SO_2NHAg$; these salts do not have a sweet taste.

Corresponding *silver salts* of *parasulphaminebenzoic acid* are described; as also that of orthobenzoic sulphinide, $C_6H_4 < \begin{matrix} CO \\ SO_2 \end{matrix} > NAg$.

H. B.

Pseudocumene-derivatives. By W. Kelbe and K. Pathe (*Ber.*, **19**, 1546—1547).—Pseudocumenesulphonic acid is decomposed by bromine in presence of water, mainly into bromopseudocumene and sulphuric acid; the *bromosulphonic* acid, $C_6HMe_3BrSO_3H + 1\frac{1}{2}H_2O$ [Me_3 : Br : SO_3H = 1 : 2 : 4 : 3 : 5], formed in small quantities, crystallises in colourless needles which melt at 116°.

Its *sodium* salt crystallises with 1 mol. H_2O in white glistening

needles, the *potassium* salt with 1 mol. H_2O in leaflets or needles, the *lead* salt with 3 mols. H_2O is a crystalline precipitate, and the *silver* salt forms sparingly soluble micaceous leaflets.

Dinitrobromopseudocumenes, [$Me_3 : Br : (NO_2)_2 = 1 : 2 : 4 : 5 : 3 : 6$ and $1 : 2 : 3 : 4 : 5 : 6$], crystallise in minute, golden tables and leaflets respectively; the former melts at 213—214°, the latter at 180—181°; both are sparingly soluble in alcohol. The *bromosulphonic* acid,

$$[Me_3 : Br : SO_3H = 1 : 2 : 4 : 5 : 6],$$

obtained by sulphonating the bromopseudocumene melting at 75°, crystallises with 1 mol. H_2O in hard needles, softens at 105°, and melts at 121°. Its *amide* crystallises in aggregate of needles melting at 183°—184°; the *potassium* and *sodium* salts in sparingly soluble leaflets and minute tables respectively. The *pseudocumenesulphonic* acid obtained from it by hydrogenation forms a *barium* salt crystallising with 1 mol. H_2O in leaflets, a *sodium* and *potassium* salt with 1 mol. H_2O in soluble leaflets, and an amide in thick prisms melting at 178—179°.

Tetramethylbenzene, $C_6H_2Me_4$ [$= 1 : 2 : 3 : 4$], prepared by methylation of pseudocumene at a high pressure, or preferably by hydrolysis of its sulphonic acid, is a colourless, aromatic liquid boiling at 170—190°. The *sodium* salt of its *sulphonic* acid crystallises with 1 mol. H_2O in delicate needles, and the *amide* in hard prisms melting at 177°, insoluble in water, readily soluble in alcohol and benzene.

V. H. V.

Synthesis of Indole-derivatives. By E. Fischer (*Ber.*, **19**, 1563—1570).—Indole-derivatives are readily obtained by heating with zinc chloride the primary and secondary aromatic hydrazine compounds of all saturated ketones and ketonic acids containing a methyl or methylene-group, and of all aldehydes containing a methylene-group.

Methylketole is obtained by heating acetonephenylhydrazine with five times its weight of zinc chloride at 180°.

Dimethylindole, $C_6H_4<\overset{CMe}{NH}>CMe$, prepared from the phenylhydrazine compound of methyl ethyl ketone, melts at 106°, does not show the pine-wood reaction, and by treatment with nitrous acid is converted into the nitrosamine, $C_8NH_4Me_2{\cdot}NO$; this is reconverted into dimethylindole by the action of stannous chloride.

Methylethylindole, $C_6H_4<\overset{CEt}{NH}>CMe$, prepared from the phenylhydrazine compound of methyl propyl ketone, is liquid, distils unaltered, and gives an oily nitrosamine.

Dimethylindole, $C_6H_4<\overset{CH}{NMe}>CMe$, melting at 56°, and methylphenylindole, $C_6H_4<\overset{CH}{NMe}>CPh$, melting at 100—101°, are obtained from the compounds of methylphenylhydrazine with acetone and with acetophenone respectively; both give the pine-wood reaction.

The phenylindole, prepared from acetophenone phenylhydrazine, is identical with the α-phenylindole of Pictet (this vol., p. 711).

Diphenylindole, $C_6H_4<\begin{matrix}CPh\\NH\end{matrix}>CPh$, is prepared from desoxybenzoïn phenylhydrazine either by heating with zinc chloride or by warming in alcoholic solution with hydrochloric acid. It melts at 122—123°, distils unaltered, and does not give the pine-wood reaction.

Skatole was obtained from the phenylhydrazine-derivative of propaldehyde; homologous compounds are formed from the hydrazine compounds of valeraldehyde and œnanthaldehyde, but are not described.

By the action of phenylhydrazine on acroleïn, a crystalline substance of the formula $C_9H_{10}N_2$ is obtained; it does not yield an indole-derivative when fused with zinc chloride, and is probably closely related to Knorr's pyrrazoles.

Indolecarboxylic acid, $C_6H_4<\begin{matrix}CH\\NH\end{matrix}>C\cdot COOH$, is obtained as its ethyl or methyl salt by heating the phenylhydrazine-derivative of ethyl or methyl pyroracemate with zinc chloride at 195—200°. The free acid crystallises in long, slender needles, melts at about 200°, partly subliming and partly decomposing into indole and carbonic anhydride at the same time. It is moderately soluble in water, readily in alcohol and ether.

Methylindoleacetic acid, $NH<\begin{matrix}C_6H_4\\CMe\end{matrix}>C\cdot CH_2\cdot COOH$, is prepared by heating phenylhydrazinelevulinic acid melting at 108° (*Ber.*, **16**, 2243), with zinc chloride at 135—140°. It melts at 195—200° with evolution of carbonic anhydride and conversion into the dimethylindole obtained from methyl ethyl ketone. If the above phenylhydrazine-derivative is heated alone at 170°, it is converted into an anhydride, $C_{11}H_{12}N_2O$, melting at 107°. *Dimethylindole acetic acid*, $NMe<\begin{matrix}C_6H_4\\CMe\end{matrix}>C\cdot CH_2\cdot COOH$, is obtained as its ethyl salt from the compound of methylphenylhydrazine and ethyl levulinate. The free acid melts at 186° and decomposes at higher temperatures into carbonic anhydride and *trimethylindole*, $C_8NH_4Me_3$; this is liquid, boils without decomposition, and does not colour pine-wood.

Dimethylindolecarboxylic acid, $NMe<\begin{matrix}C_6H_4\\CMe\end{matrix}>O\cdot COOH$, prepared from the compound of methylphenylhydrazine with ethyl acetoacetate, melts at 200° with decomposition into carbonic anhydride, and that dimethylindole which is also obtainable from acetone.

In conclusion, it is pointed out that all indole compounds derived from primary hydrazines contain an imide-group, and that the pine-wood reaction is no longer obtainable if both the carbon-atoms of the indole-ring are combined to alkyl-groups, or if one is combined with carboxyl. A. J. G.

Action of Aluminium Chloride on the α-Monohaloïd Naphthalene Compounds. By L. Roux (*Bull. Soc. Chim.*, **45**, 510—521).—When α-bromonaphthalene dissolved in carbon bisulphide is heated with 15 to 20 per cent. of aluminium chloride at 44° for about an hour, the mixture blackens very much, and β-bromonaphthalene

is formed accompanied by some tarry matters and a small quantity of naphthalene and dibromonaphthalenes. *β-Bromonaphthalene* crystallises in the rhombic system, forming small, lustrous, pearly scales; its sp. gr. = 1·605 at 0°; it melts at 59° and boils at 280—285°; with picric acid it forms a compound crystallising in slender, yellow needles and melting at 79°.

An unsuccessful attempt was made to prepare β-bromonaphthalene directly from naphthalene by the addition of bromine in the presence of aluminium chloride, the α-compound is, however, alone formed, although on further heating it is finally converted into the β-compound.

On heating α-chloronaphthalene in carbon bisulphide with aluminium chloride on the water-bath for two hours, the mixture blackens and a small portion is converted into the β-compound.

α-Iodonaphthalene when treated in a similar manner with aluminium chloride is not converted into the β-compound, but iodine is set free and naphthalene and some tarry matters obtained.

If a mixture of α-bromonaphthalene and toluene is heated with aluminium chloride, naphthalene and a mixture of bromotoluenes is formed; when the toluene is replaced by benzene a similar reaction takes place. A. P.

Naphthalene-derivatives. By I. Guareschi (*Gazzetta*, **16**, 142—153).—Laurent and Glaser have described a dibromonaphthalene tetrabromide crystallising in rhombic tables or prisms. It is here shown that this substance is a mixture of two or more isomerides separable by fractional crystallisation from ether, and subsequently from chloroform into a portion with a definite melting point, 173—174°, and two other portions melting at about 97—100° and 119—120°. The first crystallises in colourless prisms, insoluble in water, sparingly soluble in alcohol and ether, readily soluble in benzene and chloroform. Treated with sodium ethoxide it yields a tetrabromonaphthalene melting at 175°, crystallising in needles or prisms and yielding on oxidation dibromophthalide and tetrabromonaphthaquinone; its constitution is thus probably [Br : Br : Br : Br = 2 : 3 : 1′ : 4′]. Both the other portions of the dibromonaphthalene tetrabromide yield a tetrabromonaphthalene which melts at 119—120°, and crystallises in small colourless needles, soluble in ether and benzene. The *tetrabromonaphthaquinone* mentioned above [O_2 : Br_4 = 1 : 4 : 2 : 3 : 1′ : 4′], crystallises in orange-yellow prisms melting at 224—225°, sparingly soluble in cold, readily in hot alcohol. A brief description is also given of similar experiments with the chloronaphthalenes—to be described in a future memoir. V. H. V.

Conversion of Naphthalene-derivatives into Substituted Phthalides. By I. Guareschi (*Ber.*, **19**, 1154—1157).—*Paradichloronaphthaquinone*, $C_{10}H_4Cl_2O_2$ [Cl_2 = 1′ : 4′], is prepared by warming a glacial acetic acid solution of β-dichloronaphthalene with chromic acid on the water-bath for 30 minutes. It crystallises in long, yellow needles, is practically insoluble in water, but dissolves readily in ether, melts at 173—174°, and sublimes in fine needles;

soda converts it into chloroxynaphthaquinone which is precipitated in reddish flocks on the addition of an acid. It combines with phenylhydrazine, forming a coloured mass, soluble in alcohol to a reddish-violet solution; it also combines with aniline, forming *chloronaphthaquinoneanilide*, $NHPh{\cdot}C_{10}H_4ClO_2$, which crystallises in garnet-red needles, and melts at 183—185°.

On evaporating to dryness the mother-liquor of paradichloronaphthaquinone and treating the solid residue with water, a whitish crystalline powder consisting of *paradichlorophthalide*, $C_8H_4Cl_2O_2$ [Cl_2 = 1 : 4], remains; this crystallises from alcohol in short prisms or flat needles, melts at 163°, and sublimes unaltered; it is very sparingly soluble in water, but dissolves readily in alcohol or ether, forming neutral solutions; it is also soluble in aqueous potash or soda from which hydrochloric acid precipitates it unaltered; it is a very stable compound, does not reduce ammoniacal silver nitrate, and does not form any colouring matter with phenol and sulphuric acid; it does not unite with hydroxylamine hydrochloride or phenylhydrazine.

A. P.

Derivatives of Camphor. By L. Balbiano (*Gazzetta*, **16**, 132—139).—In a former paper (this vol., p. 72) the author has shown by means of the phenylhydrazine reaction that camphor contains a carbonyl-group. Camphophenylhydrazine is an oil readily decomposed, even when boiled under reduced pressure. In ethereal solution it is converted by hydrogen chloride into aniline hydrochloride and the nitrile of campholenic acid (compare Goldschmidt and Zürrer, Abstr., 1884, 1364), thus: $C_{10}H_{16}{\cdot}N_2HPh + HCl = C_9H_{15}{\cdot}CN + NH_2Ph,HCl$. When distilled with concentrated hydrochloric acid it yields the same products together with camphor and phenylhydrazine hydrochloride, thus: $2C_9H_{16}N_2HPh + 2HCl + H_2O = C_9H_{16}CO + C_9H_{15}{\cdot}CN + NH_2NHPh,HCl + NH_2Ph,HCl$. The reaction between bromocamphor and phenylhydrazine is very violent; to modify it the temperature must be lowered and the solvents perfectly dried. Under these conditions phenylhydrazine hydrobromide is formed together with a derivative of dihydrazine, which it is proposed to designate *camphylphenyldihydrazine*. This compound, $N_2H_2Ph{\cdot}C_{10}H_{15}{\cdot}N_2HPh$, is a solid, amorphous substance, melting at 55°, soluble in alcohol and ether, insoluble in water. The reaction leading to its formation is as follows: $C_{10}H_{15}BrO + 3PhHN_2H_2 = N_2H_2Ph{\cdot}C_{10}H_{15}{\cdot}N_2HPh + PhN_2H_3,HBr + H_2O$.

V. H. V.

Solubility of Chitin. By C. F. W. Krukenberg (*Zeit. Biol.*, **22**, 480—488).—The solution of chitin in concentrated hydrochloric acid is not a simple one like that of sugar in water. During the first hour of the action of this acid, a chitin chloride is formed which swells up in the acid; on filtering, a cloudy filtrate is obtained, which contains about 2 per cent. of chitin precipitable by water or baryta-water. The filtrate, moreover, on heating does not yield glucosamine hydrochloride or other products of decomposition. After longer action of the acid, a partial or complete dissociation of the chloride first formed occurs; a clear fluid and a jelly-like residue being distinguishable; the filtrate yields 1 to 2 per cent. of dry residue, consisting mostly

of a dextrin-like substance with small reducing power; only very small quantities of chitin, precipitable by water, and of glucosamine hydrochloride being present. The action of 5 and 10 per cent. solutions of sodium and potassium carbonates saturated with chlorine is to convert chitin into a substance corresponding to amidulin. A small amount of chitin had entered into solution at the end of 12 days; it was filtered; the filtrate was colourless and gave a dry residue of 0·15 to 0·32 per cent. after the salts had been dialysed away. This residue dissolved easily in cold water, reduced alkaline copper solutions on heating, and gave copious precipitates insoluble in excess, with both neutral and basic lead acetate. These precipitates and its indiffusibility distinguish this substance from glucosamine hydrochloride. It is a compound of glucosamine hydrochloride, and a more feebly reducing substance, probably a carbohydrate resembling dextrin. After some months it undergoes dissociation; water dissolving from it glucosamine hydrochloride, the residue consisting of a feebly reducing dextrin-like carbohydrate, which, however, gives no colour with iodine. The chitin which remains undissolved by the action of the alkaline hypochlorites is altered mechanically, having a paraffin-like appearance; it swells up in water, is coloured faintly red by iodine, and when boiled with caustic soda decomposition products are formed which colour the liquid yellow. After prolonged dialysis, it was dried on the water-bath, and it then began to form decomposition products easily soluble in water; these being removed by water, the residue was dried over H_2SO_4, and was found to behave to hydrochloric acid like ordinary chitin. W. D. H.

Bitter Principle of the Hop. By H. Bungener (*Bull. Soc. Chim.*, **45**, 487—496).—A bitter principle which the author designates *lupulic acid*, $C_{50}H_{70}O_8$, may be obtained from hops by extracting with light petroleum and purifying by repeated recrystallisation. It forms colourless, prismatic crystals, melts at 92—93°, and is readily soluble in the usual solvents with the exception of water; on treating its ethereal solution with an aqueous solution of copper acetate, *copper lupulate*, $C_{50}H_{68}O_8Cu$, is precipitated as a green, crystalline powder. The author was unable to obtain the salts of potassium, sodium, calcium, and barium, in the crystalline form; the salts of the alkalis are very soluble in water, whilst those of calcium and barium are insoluble in water but dissolve in alcohol. Lupulic acid reduces ammoniacal silver solutions, it is also rapidly oxidised by the air, being converted into an amorphous, yellow, resinous compound, very similar in its properties to the unaltered acid, a small amount of valeric acid and aldehyde being formed at the same time; it is probable that the unpleasant odour of old hops is due to this. The oxidised resinous product is soluble in water (0·3 gram per litre), forming a very bitter, yellow solution from which it is precipitated on the addition of sulphuric acid. It is to this resinous compound that the bitterness of beer is due; in aqueous infusions of hops, however, a considerable amount of the unaltered lupulic acid is present, dissolved in minute floating globules of oil.

The resinous oxidation product of lupulic acid has an antiseptic

action on the lactic acid ferment, but the various saccharomyces and the acetic acid ferment are unaffected by it. A. P.

Blue Colouring Matter of Decaying Wood. By S. Rideal (*Chem. News*, **53**, 277—278).—The blue colouring matter formed in decaying birch wood (*Betula alba*) is soluble in chloroform and glacial acetic acid to a fine blue solution; potash changes it to brown, but on acidifying the blue colour returns. On evaporating the chloroform solution, a blue, amorphous mass is left, soluble in glacial acetic acid but turned brown by concentrated hydrochloric acid. The acetic solution loses its blue colour after a time or on warming, hence on partial evaporation, a brown residue is obtained; this residue gives a brown precipitate in water, insoluble in chloroform or carbon bisulphide but soluble in glacial acetic acid, potash or ammonia yielding a yellowish-brown solution; when acidified with hydrochloric acid the alkaline solutions give a bright blue precipitate. The colouring matter is non-nitrogenous and is destitute of mineral matter, the blue colour is destroyed by reducing agents, but may be restored by careful treatment with nitric acid. The chloroform solution exhibits a faint but distinct absorption-band in the spectrum, situated between the C and D lines. Coniferin has not been detected in birch wood. Moreover, comparative experiments establish the distinction of this blue colouring matter from that found in decaying Canadian balsam pine wood (*Abies balsamea*), and from that produced by the action of sulphuric acid on coniferin. It is suggested that its origin may probably be traced back to the action of an organism.

D. A. L.

Transformation of Pyrroline into Pyridine. By G. Ciamician (*Gazzetta*, **16**, 140—141).—The formation of monochloro- and monobromo-pyridine from potassium pyrroline by the action of chloroform and bromoform respectively, observed by the author in association with Dennstedt (Abstr., 1882, 867 and 1214), is capable of two explanations. It may be considered firstly that a CCl-grouping is introduced as such, thus: $C_4H_4NK + CHCl_3 = C_4H_4NCCl + KCl + HCl$; or secondly, the CH-grouping of the chloroform remains intact, whilst there is an interchange between the chlorine of the chloroform and the hydrogen of the pyrroline, thus: $C_4H_4NK + CHCl_3 = C_4H_3ClN{\cdot}CH + KCl + HCl$. The former explanation was preferred by the author, inasmuch as carbon tetrachloride yields the same chloropyridine as chloroform. But as Weidel has subsequently shown that in the homopyridine of Hofmann, which is identical with the bromopyridine from pyrroline, the position of the bromine is the same as that of the carboxyl in nicotinic acid [N : Br = 1 : 3], the author now inclines to the second explanation, as more in accordance with the above constitution of the bromopyridine. V. H. V.

Constitution of some Quinoline-derivatives. By Z. H. Skraup and P. Brunner (*Monatsh. Chem.*, **7**, 139—157).—Metamidotoluene when subjected to Skraup's reaction, yields (like several other meta-derivatives) two isomeric methyl-quinolines. These were separated by crystallisation of their hydrogen sulphates from alcohol. The base

whose sulphate crystallises out first, occurs in by far the larger quantity; it boils at 250°; the platinochloride, $(C_{10}H_9N_2)_2H_2PtCl_6 + 2H_2O$, melts at 223—224°; the picrate melts at 237°; the chromate melts at 88—90°, and is sparingly soluble in hot water. It has the constitution C_9NH_6Me [Me = 2].

The second base boils at 250—252°; its platinochloride,

$$(C_{10}NH_9)_2PtCl_6 + 2H_2O,$$

melts at 223—224°; the picrate melts at a far lower temperature than that of the first base, and the chromate is readily soluble.

Quinolinecarboxylic acid, $C_9NH_6{\cdot}COOH$ [COOH = 2], is obtained by oxidising the first base with chromic acid under pressure. It crystallises in slender needles, melts at 247°, is sparingly soluble in cold water, only gives a very pale coloration with ferric chloride, and none with ferrous sulphate, and yields quinoline when heated with lime. The hydrochloride, $C_{10}H_7NO_2,HCl + H_2O$, crystallises in triclinic prisms, $a : b : c = 0{\cdot}4493 : 1 : 0{\cdot}3774$. The platinochloride, $(C_{10}H_7NO_2)_2,H_2PtCl_6$, crystallises in large, thick, dark orange-red, monoclinic prisms, $a : b : c = 0{\cdot}6923 : 1 : 0{\cdot}6026$. This acid thus differs from the six quinolinecarboxylic acids previously known, and completes the group of these acids, seven being indicated by theory. As this acid is obtained from metamidotoluene by the glycerol reaction, &c., the COOH-group must be in either the 2 or the 4 position, the acid prepared from metamidobenzoic acid by Skraup's reaction, having its COOH-group in the complementary position. The formation of the latter acid from 1, 4 quinolinedicarboxylic acid shows, however, that in it COOH = 4; therefore the new acid must have the constitution [COOH = 2].

1, 4 *Quinolinedicarboxylic acid*, $C_9NH_5(COOH)$, is prepared by heating amidoterephthalic acid, orthonitrophenol, glycerol, and sulphuric acid, at 160—180° for one hour. It crystallises in long needles, is very sparingly soluble in cold water, melts at 268—270°, and decomposes at a slightly higher temperature. The hydrochloride, $C_{11}H_7NO_4,HCl + 1\frac{1}{2}H_2O$, crystallises in microscopic, four-sided tables; the platinochloride, $(C_{11}H_7NO_4)_2,H_2PtCl_6$, forms a yellowish-red, crystalline powder. When the acid is heated at 170—180° it loses carbonic anhydride, and is converted into a mixture of 1 and 4 quinolinecarboxylic acids, the latter greatly preponderating. A. J. G.

Syntheses in the Quinoline Series. By F. Just (*Ber.*, **19**, 1462—1466).—*Phenylhydroxyquinolinecarboxylic acid*,

$$OH{\cdot}C_9NH_4Ph{\cdot}COOH, [Ph : COOH : OH = 2' : 3' : 4'],$$

is obtained from its ethyl salt (this vol., p. 161) by saponification, &c. It is crystalline, melts at 232°, loses carbonic anhydride when heated above its melting point, is readily soluble in acetic acid, sparingly soluble in hot water or boiling alcohol, nearly insoluble in ether and cold water. The calcium and silver salts are described.

Phenyhydroxyquinoline, $C_9NH_5Ph{\cdot}OH$, [Ph : OH = 2' : 4'] is obtained from the acid above described by heating above its melting point or by heating its ethyl salt with hydrochloric acid under

pressure. It crystallises in colourless plates, melts at 253°, and yields salts with both acids and bases. A. J. G.

Syntheses in the Quinoline Series. By F. Just (*Ber.*, **19**, 1541—1545; compare this vol., p. 161).—*Ethyl phenylhydroxyparatoluquinoline carboxylate*, $OH{\cdot}C_9NH_3MePh{\cdot}COOEt$ [= 4′ : 4 : 2′ : 3′], is obtained by heating ethyl paratolubenzenylmalonate (from ethyl sodomalonate and benzoylparatoluidimide chloride, this vol., p. 617) at 160°. It crystallises from alcohol in long, slender, colourless needles, melting at 236° and it dissolves in strong hydrochloric acid with formation of an unstable *hydrochloride*. The *free acid* is prepared by boiling the ethyl salt with an excess of caustic potash. It forms a voluminous precipitate consisting of slender needles, dissolves rather readily in hot glacial acetic acid, and is almost insoluble in water, alcohol, and ether. When heated at 250° it gives off 1 mol. of carbonic anhydride and yields *α-phenyl-γ-hydroxyparatoluquinoline*, $C_9NH_4MePh{\cdot}OH$. The latter is more conveniently prepared by heating the ethyl salt of the acid with moderately strong hydrochloric acid at 150°. It crystallises from alcohol in lustrous plates melting at 291°. It has the properties of a base and of a phenol.

Ethyl α-phenyl-γ-hydroxyorthotoluquinolinecarboxylate,

$$OH{\cdot}C_9NH_3MePh{\cdot}COOEt\ [= 4' : 1 : 2' : 3'],$$

is obtained by heating the product of the reaction between ethyl sodomalonate and benzoylorthotoluidimide chloride (*loc. cit.*) at 170°; it melts at 208·5°. N. H. M.

Synthesis of Isoquinoline. By S. Gabriel (*Ber.*, **19**, 1653—1656).—The author has employed a similar method to that used by him (this vol., pp. 265 and 630) for synthesising phenylisoquinoline. As the compound $COOH{\cdot}C_6H_4{\cdot}CH_2{\cdot}COH$, which should form the starting point, is unknown, the author employed the corresponding dicarboxylic acid, $COOH{\cdot}C_6H_4{\cdot}CH_2{\cdot}COOH$, described by Hlasiwetz and Barth, Schreder, W. Wislicenus, and others. When the ammonium salt of this acid was heated, ammonia and water were evolved, and *homo-orthophthalimide*, $C_6H_4{<}\begin{matrix}CH_2{\cdot}CO\\CO{\cdot}NH\end{matrix}{>}$, obtained. This forms colourless needles, sparingly soluble in alcohol, more easily in acetic acid, melts at 233°, and distils almost unchanged. When heated with phosphoric oxychloride at 150—170° it yields *dichlorisoquinoline*, $C_6H_4{<}\begin{matrix}CH : CCl\\CCl : N\end{matrix}{>}$ which crystallises from alcohol in long, flat needles, melting at 122—123°. It sublimes slowly at 100°, has a peculiar sweetish odour, but does not show basic properties. When heated for three hours at 170° with hydriodic acid and amorphous phosphorus it yields *monochlorisoquinoline*, C_9NH_6Cl; this crystallises in long, colourless needles, melts at 45° and dissolves readily in acids but its salts are decomposed by water. If the dichloro-compound is heated for a long time with amorphous phosphorus at 200° it yields isoquinoline. L. T. T.

Morphine Lactate. By D. B. Dott (*Pharm. J. Trans.* [3], **16**, 958—959).—Morphine lactate crystallises from water in four-sided prisms of the composition $C_{17}H_{19}NO_3,C_3H_6O_3$. At 15·5° one part of the salt dissolves in eight parts of water, or in 93 parts of 85 per cent. alcohol. Heated at 110° it very slowly undergoes decomposition, losing weight and darkening in colour. D. A. L.

Thebaïne. By W. C. Howard and W. Roser (*Ber.*, **19**, 1596—1604).—Former experiments by one of the authors (Abstr., 1884, 1202) have shown that thebaïne is a tertiary base, and that when heated with hydrochloric or hydrobromic acid it yields morphothebaïne together with either methyl or ethyl chloride. By repeating the experiment with hydriodic acid it is shown that methyl iodide is formed thus : $C_{19}H_{21}NO_3 + 2HI = C_{17}H_{17}NO_3 + 2MeI$. Thebaïne, $C_{17}H_{15}NO(OMe)_2$, is therefore the dimethyl ether of morphothebaïne, $C_{17}H_{15}NO(OH)_2$.

Morphothebaïne is also characterised as a tertiary base by its combining directly with the halogen-derivatives of the hydrocarbons; its *methiodide* crystallises in quadratic tables, the ethiodide in the rhombic form, and the benzochloride in small needles.

Among the products of the decomposition of thebaïne-methylhydroxide are trimethylamine, and a substance of the composition $C_{14}H_{12}O_3$, which is probably an oxy-derivative of phenanthrene.

V. H. V.

Notes on Quinine Hydrate. By Flückiger (*Pharm. J. Trans.* [3], **16**, 897) and by O. Hesse (*ibid.*, 937).—Controverting the statement of Fletcher (this vol., p. 371) that quinine hydrate contains only 1 mol. H_2O, Flückiger points out that a trihydrate is obtained by precipitating with ammonia a solution of quinine sulphate, saturated at 15°, and that it crystallises perfectly; other amorphous hydrates may however be obtained by other methods, for example: an amorphous dihydrate is precipitated by ammonia from concentrated solutions of quinine sulphate. Hesse (*loc. cit.*) confirms Flückiger's statement with regard to dilute solutions of quinine salts. Quinine trihydrate may be crystallised from ether at temperatures not above 10°, but it is more generally obtained in the amorphous state from this menstruum. The trihydrate may be exposed in the air at 15° without loss of water, but at 20° it loses 1 mol. H_2O, and when dried first at 40° then at 60°, it loses all its water. Quinine becomes perfectly anhydrous at 100°, but if partially dried at 30°, or when in the amorphous form, as generally obtained from ether, it retains a small quantity of water with great persistency. When exposed over sulphuric acid at 20°, quinine trihydrate loses all or only part of its water according to the strength of acid employed. The quinine of commerce varies in hydration, but averages 2 mols. H_2O.

D. A. L.

Cinchonidine in Quinine Sulphate. By O. Hesse (*Pharm. J. Trans.* [3], **16**, 1025—1026).—The author criticises and exposes the inconsistency of De Vrij's methods and results (compare Cownley, this vol., p. 632). It is remarked, however, that the cinchonidine may

be determined with great accuracy in presence of quinine by the optical method; but the absence of hydroquinine ($C_{20}H_{26}N_2O_2$) must first be ensured, for otherwise, as is evident from a comparison of the rotatory powers of the three alkaloïds (by Oudeman's method for concentration B; quinine tartrate, $[\alpha]_D = -212{\cdot}5°$; hydroquinine tartrate, $[\alpha]_D = -176{\cdot}9°$; cinchonidine tartrate, $[\alpha]_D = -132{\cdot}0°$), the hydroquinine will be regarded as cinchonidine, and whereas hydroquinine is therapeutically as good as quinine, cinchonidine is not. Moreover, hydroquinine is associated with quinine in the bark, and cannot be separated completely from it except by converting quinine sulphate into the acid salt and recrystallising this from water or alcohol. It is also precipitated along with the quinine by a soluble tartrate.

D. A. L.

Xanthostrychnol and Strychnol. By W. F. Loebisch and P. Schoop (*Monatsh. Chem.*, **7**, 75—94).—When xanthostrychnol (this vol., p. 269) is reduced with hydrochloric acid and stannous chloride, and the stannochloride decomposed in the usual way, a base is obtained which is identical with the amidostrychnine formed by the reduction of nitrostrychnine with tin and hydrochloric acid (this vol., p. 268), together with a minute quantity of another base. *Acetamidostrychnine*, $C_{21}H_{21}N_2O_2{\cdot}NHAc,H_2O$, forms quadratic tables melting at 205° (uncorr.). When dissolved in a little dilute sulphuric acid, and potassium dichromate added, it does not give a blue coloration, but when boiled for some time with dilute sulphuric acid it gives the colour reactions for amidostrychnine. The *hydrochloride* forms colourless tables easily soluble in water; the platinochloride is obtained as an orange-yellow precipitate. With sulphuric acid, nitric acid, acetic acid, and oxalic acid, acetylamidostrychnine also forms characteristic salts. From its reduction products xanthostrychnol cannot be an azo-compound.

When xanthostrychnol is boiled with dilute hydrochloric acid for some minutes, or when it is allowed to remain for some time in solution in strong hydrochloric acid, the addition of a slight excess of ammonia causes the precipitation of a yellow substance, which the authors have identified as nitrostrychnine. From this they conclude that the action of hydrochloric acid is to dehydrate the xanthostrychnol, and they now regard the latter as the *hydrate* of *nitrostrychnine*, $C_{21}H_{21}N_2O_2NO_2,2H_2O$. In the former paper (*loc. cit.*) they considered xanthostrychnol to be isomeric with nitrostrychnine. It was not possible to obtain compounds of xanthostrychnol with ammonia, trimethylamine, or aniline. The acid and normal barium salts of xanthostrychnol are described. Iodide of methyl gives with the potassium salt a brilliant scaly precipitate, which is converted into a cinnabar-red salt by addition of a little alkali. Xanthostrychnol can be obtained from nitrostrychnine by boiling with aqueous as well as with alcoholic potash.

Strychnol or *strychnine hydrate*, $C_{21}H_{22}N_2O_2 + 2H_2O$, is prepared by boiling strychnine with a mixture of sodium ethoxide and absolute alcohol. The strychnine dissolves with a yellow coloration. On evaporating the mixture to expel the alcohol, a brown oil remains, which in time becomes solid. On dissolving this in water and passing a stream of carbonic anhydride, strychnol separates as a slightly yellow

precipitate, which can be further purified by solution in ammonia and reprecipitation. It then forms a white, crystalline mass, consisting of microscopic, wedge-shaped needles; it does not give the strychnine reaction with potassium dichromate and sulphuric acid, but is coloured an intense carmine-red with sulphuric and nitric acids. At 150° the greater part of the water is lost, but decomposition takes place, and strychnine cannot be obtained from the residue. Strychnol is precipitated from acetic acid solution by the usual alkaloïdal reagents; it is very sparingly soluble in cold water, easily in hot. Boiled with dilute acids, or allowed to remain for some time with strong acids, it is dehydrated, and strychnine is formed. Strychnol differs from strychnine in being very readily oxidised; it even reduces an ammoniacal solution of silver oxide.

The authors point out the close relation between the colour reactions of strychnol and brucine, and also the identity of their respective actions with bromine. Strychnol gives no compounds with ammonia, trimethylamine, or aniline; it dissolves in all these, but any compound formed is dissociated on evaporation.

Strychnine when heated with aqueous potash does not yield strychnol in the same way that nitrostrychnine yields xanthostrychnol, but a substance is formed which is probably identical with Gal and Etard's *dihydrostrychnine*.

The authors have also repeated Goldschmidt's experiments, and have confirmed the formation of indole by fusing strychnine with potassium hydroxide. They also obtained evidence of the presence of butyric acid in the fused mass.

When an alcoholic solution of strychnine is reduced with metallic sodium, an additive product—strychnine hydride—is apparently formed. G. H. M.

Jaborine. By Hardy and Calmels (*Compt. rend.*, **102**, 1251—1254). —Pure dry pilocarpine does not yield jaborine when heated at 100° for six hours, neither can this substance be obtained by the action of alcoholic iodides on argento-pilocarpidine. If, however, carefully dried pilocarpine is heated rapidly to 175°, kept at this temperature for about half an hour, and the product extracted with water made alkaline with baryta, and shaken with ether, the ether contains jaborine, and the aqueous solution contains pilocarpidine and jaboric acid. *Jaborine* separates from alcohol or ether in a brown mass, which changes to a brittle, resinous solid. It is insoluble in water, but dissolves readily in ether, and is also soluble in jaboric acid. From solutions of the hydrochloride it is thrown down by potash as a curdy precipitate, which readily agglomerates under warm water. When boiled with concentrated aqueous potash it is converted into pilocarpidine.

Jaborine hydrochloride is extremely soluble in water and alcohol. When boiled with excess of hydrochloric acid, it is converted into pilocarpidine hydrochloride. Solutions of jaborine are brown with a greenish fluorescence, which is not completely removed by animal charcoal. An alcoholic solution of free jaborine yields with a limited quantity of platinic chloride, a dirty white, gelatinous precipitate of

the composition $(C_{22}H_{32}N_4O_4)_2,PtCl_4$; with platinic chloride in excess, a yellowish-white precipitate of the composition $C_{22}H_{32}N_4O_4,PtCl_4$, and with auric chloride a precipitate of the composition $C_{22}H_{32}N_4O_4,2AuCl_3$. In presence of a slight excess of hydrochloric acid, platinic chloride, whether in excess or otherwise, precipitates the compound

$$C_{22}H_{32}N_4O_4,H_2PtCl_6.$$

Jaboric acid is separated from pilocarpidine by precipitating with excess of silver nitrate, which forms a curdy precipitate of the composition $C_{19}H_{24}N_3O_5Ag,AgNO_3$. Jaboric acid resembles jaborine in appearance, but is very soluble in water, and is not removed from its aqueous solution by ether. With alkalis it forms gummy salts, which dissolve in water and alcohol, and are not decomposed by carbonic anhydride. With silver nitrate in limited quantity it forms the compound $C_{19}H_{24}N_3O_5Ag$, which is precipitated by alcohol in the form of a brown powder. Hot concentrated potash or boiling hydrochloric acid converts jaboric acid into pilocarpidine and β-pyridine-α-lactic acid. Alcoholic solutions of jaboric acid give with platinic chloride in limited quantity a viscous precipitate of the compound

$$(C_{19}H_{25}N_3O_5)_2,PtCl_4;$$

with platinic chloride in excess, a yellow precipitate of a hemiplatinochloride, $(C_{19}H_{25}N_3O_5)_2,PtCl_4 + 2C_{19}H_{25}N_3O_5,PtCl_4$. With auric chloride a diaurochloride, $C_{19}H_{25}N_3O_5,2AuCl_3$, is formed. The hydrochloride and nitrate of jaboric acid are viscous substances; an aqueous solution of the former gives a viscous precipitate of the composition $(C_{19}H_{25}N_3O_5)_2,H_2PtCl_6$, with a limited quantity of platinic chloride.

Jaborine and jaboric acid are products of the condensation of pilocarpine, this condensation taking place on the betain nucleus, and may be thus represented (Py = pyridyl):—

$$NMe_3\begin{matrix}<\text{CMePy}^{\beta}\cdot\text{CO}\cdot\text{O}\\ \text{O}\cdot\text{CO}\cdot\text{CMePy}^{\beta}>\end{matrix}NMe_3.$$

Jaborine.

$$OH\cdot CMePy^{\beta}\cdot CO\cdot O\cdot NMe_3\cdot CMePy^{\beta}\cdot COOH.$$

Jaboric acid.

C. H. B.

Piliganine, an Alkaloïd. By Adrian (*Compt. rend.*, **102**, 1322—1323).—The *Piligan* is a Brazilian lycopod, which resembles *L. Selago*, and is probably the variety *L. Saussurus*.

Piliganine forms a soft, yellowish, transparent mass, with an odour recalling that of pelletierine. It has an alkaline reaction, and gives white fumes with hydrochloric acid. It dissolves in water, alcohol, and chloroform, but is only slightly soluble in ether. The hydrochloride forms highly deliquescent, microscopic crystals. Solutions of piliganine give the following reactions:—Sodium phosphomolybdate, yellowish-white precipitate; iodine solution, pale-brown precipitate; tannin, white precipitate; mercuric potassium iodide, bulky white curdy precipitate; mercuric chloride and platinum chloride, no reaction; picric acid, yellowish, crystalline precipitate after some time.

Piliganine is very poisonous, and has a distinct emeto-cathartic action. C. H. B.

Choloïdanic and Pseudocholoïdanic Acids. By P. Latschinoff (*Ber.*, **19**, 1521—1528).—The author previously (Abstr., 1880, 56) ascribed to Redtenbacher's choloïdanic acid the name cholecamphenic acid, believing it to be an isomeride of camphenic acid; he also mentioned (Abstr., 1880, 722) that it yields cholanic acid with elimination of water, and that cholanic acid when treated with nitric acid is reconverted into cholecamphenic acid. On the other hand, Cléve (*Bull. Soc. Chem.*, **38**, 131), by the action of nitric acid on cholanic acid, obtained a compound, $C_{16}H_{24}O_7$, having the composition and properties of Redtenbacher's choloïdanic acid.

1 gram of cholanic acid was boiled with 30 c.c. of nitric acid (sp. gr. 1·28) until it was all dissolved; choloïdanic, pseudo-choloïdanic, and, in smaller quantity, other acids were obtained. The crystalline portion of the product is unaltered cholanic acid. The latter is not formed in the etherification of choloïdanic acid as previously suggested.

When the normal ethyl salt obtained by the action of ethyl iodide on silver choloïdanate is warmed with sodium carbonate solution, it is converted into the compound $C_{50}H_{71}Et_5O_{22}$; this separates from its solution in alcohol in soft, badly formed crystals, which melt at 150—170°, and decompose at 200°. The *barium* and *silver salts* were prepared. When the above-mentioned ethyl salt is warmed with sulphuric acid, it is completely saponified; the product has all the properties of choloïdanic acid. These results point to the formula $C_{25}H_{38}O$ as the most probable for choloïdanic acid.

The impure pseudocholoïdanic acid obtained as described above was purified by successive conversion into the lead, ethyl, and barium salts; the latter was again converted into the lead salt, from which the pure acid was obtained by treatment with hydrogen sulphide. It is soluble in boiling water, more soluble in boiling alcohol, from which it separates in nodular groups of microscopic hair-like needles; it does not melt at 250°. Analyses point to the formula $C_{25}H_{36}O_{10} + \frac{1}{4}H_2O$, which is that of an anhydride or lactide of choloïdanic acid. The barium and silver salts were analysed. *Ethyl pseudocholoïdanic acid*, $C_{25}H_{34}Et_2O_{10} + \frac{1}{4}H_2O$, is readily soluble in alcohol, from which it separates on the addition of water in needles which melt at 245—247°. The *barium salt* was prepared. *Methyl pseudocholoïdanic acid*,

$$C_{25}H_{32}Me_2O_{10},$$

forms groups of needles melting at 194—196°. The *normal methyl salt*, $C_{25}H_{32}Me_4O_{10}$, is prepared by the action of methyl iodide on the silver salt; it crystallises from alcohol in flat needles melting at 127—128°. N. H. M.

Isocholanic and Isobilianic Acids. By P. Latschinoff (*Ber.*, **19**, 1529—1532, comp. Abstr., 1882, 873).—The crude cholanic acid obtained by the oxidation of cholic acid (this vol., p. 566) contains 7—8 per cent. of isocholanic acid, which is separated by means

of the sparingly soluble barium salt. The free acid melts at 247—248° (not 239° as previously given, *loc. cit.*). The *ethyl salt*, $C_{25}H_{35}Et_3O_7$, is formed by the action of ethyl iodide on the silver or lead salt; it crystallises from weak alcohol in flat needles melting at 43—50°. The *methyl salt* forms plates melting at 135—136°; it is more sparingly soluble than the ethyl salt. When warmed with sodium carbonate solution, *sodium methylisocholanate* is formed.

Isobilianic acid is also present in the product of the oxidation of cholic acid; the yield of crude substances is 7—8 per cent. It crystallises from dilute alcohol in flat needles, and melts at 234—237° with decomposition. Its solubility resembles that of isocholanic acid. The *hydrogen potassium salt* forms lustrous, rhombic plates; the *normal barium* and the *silver salts* are amorphous. The *normal methyl salt* crystallises in needles which melt at 98°. N. H. M.

Gelatin. By P. Schützenberger (*Compt. rend.*, **102**, 1296—1299).—When gelatin or osseïn is heated at 200° with barium hydroxide solution, one-fifth of the total nitrogen is converted into ammonia, and carbonic anhydride and oxalic acid are also formed, these compounds and the ammonia being in the ratio of the products of decomposition of urea and oxamide. The other products are amido-acids of the acetic series, the most abundant being, in the order of their importance, glycocine, alanine, amidobutyric acid, leucine and amidocaproic acid, and acids of an homologous series, $C_nH_{2n}N_2O_5$, the value of n varying from 8 to 10.

The acids of the series $C_nH_{2n}N_2O_5$ constitute an important part of the products. They are difficult to isolate in a state of purity, dissolve very readily in water and in cold absolute alcohol, and form a thick syrup which becomes somewhat coloured during evaporation even in a vacuum, and eventually solidifies to a mass of flattened needles. When dried at 100—120°, the acids are converted into anhydrides of the formulæ $C_nH_{2n-2}N_2O_4$ and $C_{2n}H_{2n-4}N_4O_9$. They do not yield derivatives with acetic anhydride, but with ethyl iodide in presence of an alkali they yield diethyl-derivatives: syrupy substances with a bitter taste, soluble in water and alcohol. When the latter are heated with zinc-dust at 330° in a current of hydrogen, they yield a liquid with the composition and general properties of the hydropyrrolic bases (C_5H_7N and C_6H_9N). No similar compounds are obtained when the amido-acids of the acetic series are treated in the same way. It would seem that the acids $C_nH_{2n}N_2O_5$ contain nitrogen in the form of the imido-group.

The general results lead to the conclusion that osseïn is formed by the combination, with elimination of water, of 1 mol. urea or oxamide, 2 groups $C_nH_{2n}N_2O_5$, and 4 groups $C_nH_{2n+1}NO_2$ (n being 2, 3, 4, or 6 with a mean value of 3·5). The constitution of osseïn would therefore be represented by the formula—

$$C_2O_2[N(CO\cdot C_nNH_{2n}\cdot NH\cdot C_mH_{2m}\cdot NH\cdot C_pH_{2p}\cdot COOH)_2]_2.$$

C. H. B.

Globulin and Globuloses. By W. Kühne and R. H. Chittenden (*Zeit. Biol.* **22**, 409—422).—Globulin obtained from ox serum by

Hammarsten's method, was digested by pepsin with great difficulty; a large undigested residue being coagulable by the addition of acid and boiling. In that portion which underwent digestion, some was precipitable by neutralisation (parapeptone), and the rest converted into peptone; to the intermediate products in this latter process, the name *globulose* is given. Adopting the same methods used in the separation of albumoses, three kinds of globulose can be distinguished, namely: (1) *protoglobulose*, which resembles protoalbumose, except that its solution in weak sodium chloride becomes cloudy on boiling, and clear again on cooling, which is the reverse to what occurs in the case of protoalbumose; (2), *deuteroglobulose*, which differs from deuteroalbumose only in not being precipitable by sodium chloride in an acid solution; and (3), *heteroglobulose*, which has the same properties as heteroalbumose.

The following table contrasts the percentage composition of these substances with that of two varieties of albumose:—

	Proto-globulose.	Deutero-globulose.	Hetero-globulose.	Hetero-albumose.	Hemi-albumose from urine.
C	51·57	51·52	52·10	50·88	52·13
H	6·98	6·95	6·98	6·89	6·83
N	16·09	15·94	16·08	17·08	16·55
S	2·20	1·86	2·16	1·23	1·09(?)
O	23·16	23·73	22·68	23·92	23·40

The amount of carbon in the globuloses never sinks below 51 per cent., whilst in the albumoses it does. The percentage quantity of sulphur is higher, and of nitrogen lower, in the former than in the latter group of substances. The hemialbumose of the urine of patients suffering from osteomalacia resembles in its composition heteroglobulose, and is perhaps derived from the globulin of the blood.

Heteroglobulose when subjected to tryptic digestion yields antipeptone, no substance resembling antialbumid, no tyrosin, and only a trace of leucine; it therefore belongs to the anti-group of digestion-products. Protoglobulose, on the other hand, belongs to the hemi-group, yielding abundance of leucine and tyrosine.

The parapeptone obtained in the peptic digestion of globulin, is in great part unchanged by trypsin; a small amount of antipeptone is formed, but no leucine or tyrosine, except in one case where traces of these substances were found. W. D. H.

Peptones. By W. Kühne and R. H. Chittenden (*Zeit. Biol.*, **22**, 423—458).—Ammonium sulphate precipitates from a solution all proteïds but peptones. Peptones can in this way be obtained free from albumoses, with which they have in previous researches always been mixed. It was therefore necessary to repeat many previous experiments concerning the composition and properties of peptones. Amphopeptone, the mixture of peptones obtained in gastric digestion,

and antipeptone, from tryptic digestion, were thus examined. The result of digestion was acidified with acetic acid, saturated with ammonium sulphate, filtered, the filtrate evaporated to small bulk, and filtered from the crystals of the salt which separated; the remainder of the salt was removed by aqueous baryta, and the last traces by barium carbonate; dilute sulphuric acid was added to remove the baryta, and the barium sulphate filtered off. From the filtrate the peptones were precipitated by alcohol, redissolved, and again precipitated by phosphotungstic acid, and dried. In the case of amphopeptone, the first analyses were invalidated by adherent pepsin, and a substance designated mucin-peptone, apparently derived from the mucous membrane of the stomach; it forms a sticky, elastic precipitate with alcohol, but was not further investigated. The error due to these admixtures was obviated by saturating concentrated artificial gastric juice with ammonium sulphate; this precipitates the mucin and pepsin; pepsin alone redissolves in dilute hydrochloric acid; this solution was used as a digestive fluid; from it no mucin-peptone was obtained. The remains of the pepsin were subsequently removed by the ammonium sulphate with the albumoses.

Antipeptone was prepared both from fibrin and by the pancreas being allowed to digest itself.

The following table gives some of the results obtained in the analyses of these substances. In each case the samples had been purified by means of phosphotungstic acid. I. Amphopeptone from fibrin; II. Antipeptone from fibrin; III. Antipeptone from the pancreas:—

	C.	H.	N.	S.	O.	Ash.
I.....	48·75	7·21	16·26	0·77	27·01	3·22
II.....	46·59	6·69	18·28	0·67	27·77	3·67
III.....	44·47	7·15	17·94	0·57	29·87	2·07

Contrasted with previous analyses, the numbers obtained show about 1 per cent. less carbon, 1 per cent. more nitrogen, and 0·3 to 0·4 per cent. less sulphur. The percentage of nitrogen is greater in antipeptone, especially in that obtained from the gland, than in amphopeptone.

The following are the chief properties of pure peptone: When dissolved in water, it hisses and froths in the same way that phosphoric anhydride does; heat is at the same time evolved. Its solution in water is brown, which prevents its lævorotary power from being estimated. Its taste is somewhat cheesy, but not unpleasant. The bitter taste of artificially digested food must therefore be due to some product not yet separated, native proteïds and albumoses being almost tasteless. Peptones are not precipitated by sodium chloride in acid solutions, nor by ammonium sulphate; they are completely precipitated by tannin, iodo-mercuric iodide, phosphomolybdic acid, phosphotungstic acid, and picric acid. A 5 per cent. solution rendered faintly alkaline by soda has the following additional properties:—

Reagent.	Fibrin-antipeptone.	Fibrin-amphopeptone.
Acetic acid and ferrocyanide of potassium.	At first clear; later a trace of opalescence.	
Normal lead acetate	First drop nothing; more, well-marked opalescence.	Opalescence less marked.
Basic lead acetate	Dense opalescence.	Opalescence less dense.
Mercuric chloride.....	First drop nothing; more, dense opalescence.	Opalescence denser.
Copper sulphate (5 per cent.).	At first clear; later, a feeble opalescence, disappearing with excess of reagent.	Nothing.
Platinic chloride (5 per cent.).	Feeble opalescence with excess.	Nothing.
Chromic acid	Nothing.	Nothing.
Ferric chloride	Opalescence disappearing on small excess.	Nothing.
Ferric acetate and concentrated H_2SO_4.	Brown-red colour.	Brown-red colour.
Nitric acid	Yellow colour.	Yellow colour.
Boiling with concentrated HCl.	Colour darkens a little.	Colour darkens a little.
Millon's reagent.....	A white precipitate turning to a dirty yellow on heating.	A white precipitate turning to bright red on heating.
Buiret reaction	Well marked.	Well marked.

The most noteworthy difference in the above table is the behaviour to Millon's reagent; antipeptone never forms leucine and tyrosine in pancreatic digestion, whilst amphopeptone, which contains hemipeptone, does; antipeptone, moreover, after being subjected to the action of trypsin, yields no products which are coloured red or violet by bromine or chlorine water, as hemipeptone does. Moreover, when treated with sulphuric acid, antipeptone did not yield crystals of tyrosine; and no proof could be obtained of its presence by Hoffmann's nor by Piria's reaction. From antialbumid, similarly, no tyrosine could be obtained; whether this will prove to be a general rule for the anti-group of digestion-products the authors intend to investigate. W. D. H.

Physiological Chemistry.

Intravascular Clotting. By L. C. Wooldridge (*Proc. Soy. Soc.*, **40**, 134—135).—From the testis and thymus gland of the calf, the author has obtained a substance of proteïd character, the injection of which in sufficient quantity into the veins of an animal causes instant death, due to widespread intravascular clotting. The method of extraction of this substance is as follows: the organ finely minced is allowed to stand for some hours with distilled water; the liquid is strained off, and subjected to the action of a centrifugal machine so

long as any deposit is separated from it; the addition of acetic acid to the clear liquid produces a bulky precipitate. If this is dissolved in alkaline salt solution, and injected into the circulation, it immediately produces intravascular clotting. Experiments are quoted to show that the material which produces the coagulation disappears in the act. Previously no method had been known by which a complete fibrinous coagulation in the vessels of a living animal could be produced at will. V. H. V.

Influence of Glycerol, Sugar, and Fat on the Secretion of Uric Acid in Man. By J. Horbaczewski and F. Kanera (*Monatsh. Chem.*, **7**, 105—120).—A series of experiments were conducted on one of the authors during a period of 70 days, when the daily rations and mode of living were the same, with the exception of periods during which varying daily amounts of glycerol, sugar, and fat respectively were taken in addition to the normal food. For full details of the quality and quantity of food consumed and detailed analyses of the excreta the original paper must be consulted. The general results were:—

When glycerol is taken with the daily food a marked increase in the amount of uric acid secreted takes place; this, however, is only the case when free glycerol is taken; if it is taken combined with the fatty acids as neutral fats, it exerts no influence on the formation of uric acid.

Cane-sugar, and probably other carbohydrates, exert no direct influence on the formation of uric acid; it causes, however, a marked decrease of the secreted uric acid, due to the "albumin-retarding" action of the carbohydrates and proportional to it. This lowered secretion only continues as long as cane-sugar is taken. With the stoppage of the sugar, the normal uric acid formation does not again take place, but the entire amount of acid which was not secreted in consequence of the sugar is first passed, and then the normal quantity begins.

The neutral fats have a similar influence on the formation of uric acid to that of carbohydrates, but the after effects are different. The decrease in the amount of acid is proportional to the "albumin-retarding" action of the fat, but when the addition of fat to the diet is stopped, the secretion of uric acid returns at once to the normal amount.

Glycerol causes an increase in the amount of albumin formed in man, as it was known to do in the dog.

The authors consider that their results have an important bearing on the question of suitable diet for persons suffering from certain diseases which cause too large a secretion of uric acid.

G. H. M.

Behaviour of α- and β-Naphthol in the System. By M. Lesnik and M. Nencki (*Ber.*, **19**, 1534—1538). — According to Mauthner (*Maly's Jahresber.*, 1881, 230) α-naphthol is separated in human urine partly unchanged and partly as hydrogen naphthyl sulphate. The authors find that both α- and β-naphthol are separated as naphthyl hydrogen sulphates, but the greater part is converted in

the system into α- or β-naphtholglycuronic acid; this is precipitated from the urine by the addition of lead acetate. *β-Naphthylglycuronic acid*, $C_{16}H_{16}O_7 + 2H_2O$, forms long, colourless needles, soluble in hot water, more soluble in alcohol and ether. It melts at 150°. It is lævorotatory, $\alpha = -88°$. Mineral acids decompose it into naphthol and glycuronic acid. When exposed to air it becomes yellow. The *calcium salt* (with 2 mols. H_2O) is readily soluble in water.

α-Naphtholglycuronic acid also crystallises in long needles more soluble than the β-acid. It melts at 202—203°. When a trace of the acid is treated with sulphuric acid, the solution acquires an intense emerald colour which gradually changes to a dirty green. Penzoldt (*Arch. Exper. Path. Pharm.*, **21**, 34) has recently shown that after ingestion of 1 gram of naphthalene, human urine acquires a green colour when treated with sulphuric acid. This is probably due to the oxidation of the naphthalene in the organism to naphthol and the conversion of the latter into naphtholglycuronic acid. After prolonged use of naphthol the urine becomes dark coloured, as in the case of phenol. The difference between the behaviour of phenol and of the naphthols in the organism is that phenol separates chiefly as hydrogen phenyl sulphate, whilst the naphthols separate almost entirely as glycuronic acids. N. H. M.

Chemistry of Vegetable Physiology and Agriculture.

Reduction of Nitrates by Micro-organisms. By U. Gayon and G. Dupetit (*Station Agronomique de Bordeaux*, Nancy, 1886).—The reduction of nitrates with the production, under different circumstances, of nitrites, nitrogen oxides, and nitrogen gas has been observed, by the authors and by others, to be connected with the multiplication of certain bacteria (Mensel, *J. Pharm.*, **22**, 430; Gayon and Dupetit, *Mem. phys. et naturelles de Bordeaux* [2], **5**, 36; Schlöesing, *Compt. rend.*, **66**, 237; this Journal, 1873, 1198; Deherain and Maquenne, Abstr., 1883, 229; Munro, *Trans. Chem. Soc.*, 1886, 632). The present memoir contains a biological study of certain of these denitrifying microbes by the method of cultivations, an examination of the products and mechanism of the chemical reactions which they provoke, and a discussion of the agricultural application of the phenomena.

The reduction of nitrate to nitrite is brought about by many different microbes; in fact, if almost any boiled organic infusion containing a nitrate be exposed to the air, the first appearance of bacterial turbidity is seen to be accompanied by the production of nitrite. The whole of the nitrate may in this way be reduced to nitrite without the production of any gas; but this memoir is devoted especially to an account of two microbes which, in the presence of organic matter, decompose nitrates with production of nitrogen and nitrous oxide.

These two microbes were obtained by the authors from sewage, and they found that their multiplication and the accompanying destruction of nitrates could be prevented by heat and by antiseptics. (Chloroform and copper sulphate were perfectly effective; phenol and salicylic acid only retarded the denitrification and were destroyed by it; exactly similar results were obtained in the abstractor's experiments on well waters, *loc. cit.*, p. 671.) The authors have isolated and studied these organisms by systematic cultivations in sterilised liquids under various conditions. *Bacterium denitrificans* α, the more active of the two, is 0·4 to 0·6μ broad by 2—4μ long, of feeble refraction, and outlines not clearly visible except in stained preparations. They are in very active motion in liquids containing nitrate, and still more if a bubble of air be introduced into the solution; if cultivated in solutions free from nitrate but exposed to air a *zoogloea* rapidly forms on the surface. They multiply by sissiparity during the first days of development; afterwards 1—3 spores form in each individual. *Bacterium denitrificans* β differs little under the microscope from the preceding; it is a little larger and more refractive. These two bacteria are best distinguished by the rate of their development and by the products of their action on nitrates under comparative cultures in the same medium. They are best stained by methyl-violet and by gentianine. They are both äerobic microbes and multiply rapidly in a medium exempt from nitrates, provided it is in a thin layer freely exposed to the air, in a narrow tube they only develop at the top of the liquid, where oxygen can gain access. In a nitrated medium they are anäerobic microbes, taking oxygen from the nitrate, and they multiply throughout the whole mass of liquid, eventually forming a glairy layer at the bottom of the vessel.

B. denitrificans α denitrifies much more energetically than β; when cultivated in nitrated meat infusions, it forms nitrites, but not when cultivated in artificial solutions; β forms nitrites in both cases; α cause the production of nitrous oxide in cases where β produces nitrogen only. Most of the following observations were made with α. A temperature of 35° is very favourable to denitrification; previous heating to 70° destroys the bacteria, exposure to 60° or even 50° is prejudicial. The amount of nitrate destroyed is increased by diminishing the supply of air, and diminished when the air supply is ample; in a very thin layer of liquid it is even possible to cultivate these microbes without their acting on the dissolved nitrate. The most vigorous denitrification is produced by sowings from bacteria one or two days old; when allowed to remain in contact with the denitrified liquid the vitality rapidly diminishes, and a sowing 40 days old failed to produce any denitrification in 48 hours. In meat infusions 1 per cent. of nitre is most favourable to the activity of the denitrifying bacteria, but the action goes on, although imperfectly, in solutions containing as much as 2 per cent. In certain artificial solutions as much as 9 grams of nitre per litre per day can be decomposed. Almost any infusion containing organic matter will serve for the development of the bacteria; but meat infusion is more suitable than sewage, and an artificial solution of the following composition has been found very suitable: grams per litre, nitre, 10; citric acid, 7; asparagine, 5; potassium phosphate, 5;

calcium chloride cryst., 0·50; ferrous sulphate, 0·05; aluminium sulphate, 0·02; sodium silicate, 0·02; ammonia sufficient to neutralise.

When this sterilised liquid is sown with *B. denitrificans* α, evolution of gas commences after about 18 hours; most frequently this gas consists of nitrogen, either pure or mixed with a variable quantity of carbonic anhydride.

By exact analyses of the evolved gases, and of the fermented liquids, the authors show that the whole of the nitrogen of the nitrate is evolved as gas, and that the whole of the oxygen of the nitric acid is combined with the carbon of the organic matter to form carbonic anhydride, a portion of which may be evolved as gas, whilst the remainder combines with the potash of the nitrate to form potassium hydrogen carbonate. Some ammonia is formed, but this proceeds from the decomposition of the nitrogenous organic matter (asparagine) contained in the cultivation liquid. Organic matter is, in fact, essential to the reaction. 1 gram of nitre requires 0·148 gram of carbon or 0·273 gram of albuminoïd matter for its complete decomposition. It results from this that a liquid diluted before addition of nitrate causes a less active and perhaps incomplete decomposition of the latter.

Sometimes the evolved gas contains a large proportion of nitrous oxide; and in this case also the authors show that the nitrogen gas + nitrous oxide + carbonic anhydride account for all the nitrogen and available oxygen of the nitrate decomposed. The circumstances which favour the production of nitrous oxide are high temperatures, a small quantity of seed, and the nature of the latter. Thus *B. denitrificans* α always gives both nitrogen and nitrous oxide with the complete artificial medium, whereas β gives nitrogen only; by omitting asparagine from the liquid, α may be caused to yield nitrogen only.

Denitrification is accompanied by a very considerable rise of temperature—in meat infusions 5·45° and in the artificial medium 10° have been observed above similar liquids not undergoing fermentation.

In fact, whilst the decomposition of two equivalents of dissolved nitre into potash, nitrogen, and oxygen, is attended with an absorption of heat of 56·2 cal., the oxidation of 5 equivalents of carbon to carbonic anhydride produces 249 cal.; the combination of 2 equivalents of potash with 4 equivalents of carbonic anhydride produces another 22·2 cal., so that on balance much heat is available. The denitrifying bacteria will not develop in liquids deprived of nitrate and out of contact with air, not will they attack the organic matter under these circumstances; the authors therefore regard denitrification as a fermentation which consists in the direct burning up of organic carbon at the expense of the oxygen of a nitrate, and in order to prove that it is not a secondary action brought about by a reducing agent formed during the growth of the bacteria at the expense of the organic matter, they have made a number of experiments with *Bacillus amylobacter*. This organism provokes the butyric fermentation of saccharose, glucose, and starch with evolution of nascent hydrogen, but the authors show by several experiments that this nascent hydrogen does not reduce nitrates

added to the culture solutions, and that therefore the destruction of nitrates by arable soil, noticed by Deherain and Maquenne (*Ann. Agron.*, **9**, 6) in certain experiments with sugar solutions containing added nitre, is not due, as they supposed, to a secondary action of the hydrogen liberated during the butyric fermentation.

By sowing sterilised soil rich in humus with cultivations of *Bacterium denitrificans* α, and allowing a solution of nitrate to remain in contact with the soil, the authors show that the soil itself contains organic matter capable of supporting the life of the *Bacterium* which oxidises it at the expense of the nitrate; this action is increased by adding organic matter, such as sugar, to the water which percolates the soil, and by conducting the percolation in an atmosphere of carbonic anhydride. With a thorough circulation of air, no denitrification is produced.

The destruction of nitrates by soil observed in Schlöesing's experiments is explained by the authors as the work of bacteria similar to those with which they experimented. J. M. H. M.

Formation and Migration of Carbohydrates in Leaves. By A. F. W. Schimper (*Ann. Agronom.*, **12**, 127—135; from *Bot. Zeit.*, 1885, Nos. 47, 48, 49).—In order to observe the distribution of starch granules in the leaf under different circumstances, the author employs the following method of staining; the leaves are first soaked in alcohol, then placed from 12—24 hours in an iodised solution of chloral hydrate (8 chloral to 5 water). Under the influence of the chloral the leaves become very transparent, so that even the deep seated layers can be observed under the microscope; the starch granules swell greatly, and are stained blue, so that the smallest become visible.

Three leaves of *Impatiens parviflora* were cut longitudinally by the side of the midrib, so as to leave the larger half of the leaf attached to the plant. Both the plant and the detached portions of leaf were then placed in the dark in a damp atmosphere. The leaves opposite to the cut leaves contained at first abundance of starch. After 24 hours the starch had greatly diminished in the detached halves of the leaves, and in the halves remaining attached to the plant; the former contained much glucose, the latter about as much as the day before. At the end of five days both the detached and undetached portions of leaf were free from starch, but whereas the former were very rich in sugar, the latter contained it only at the base of the midrib. The leaves of this plant washed in water yield a diastatic ferment which speedily renders starch-paste soluble. The distribution of starch in a leaf of this plant cut in a normal condition is as follows: Much in the mesophyll and in the amylaceous layer which exists only in the midrib and veins of the first order; a little less in the cells of the "conducting sheath" of the little veins; much less in the conducting sheath of the large veins; a little in the inferior epidermis; none in the fibrovascular bundles, the superior epidermis, the extreme edge, or the serrations of the leaf.

If the leaf be stained after 24 hours' rest in darkness, the appearance is quite different. The veins down to the smallest ramifications

are free from starch, and in transmitted light appear yellow on a deep blue ground. The "conducting sheath" of even the small veins is also free from starch, and so are the cells of the mesophyll in immediate contact with this sheath. In the portions of the mesophyll farthest from the veins, the starch has hardly diminished. Thus the veins, or rather their conducting sheath of cells, constitute the road along which the glucose formed from the starch is carried away, as if by a network of open canals.

The reconversion of glucose into starch takes place with very different degrees of facility in different plants, and some plants (*Iris*, *Allium cepa*, *Galanthus*, *Ornithogalum*, *Hyacinthus*) which contain no starch are perhaps unable to effect the transformation. The author concludes that the formation of glucose always precedes that of starch, and that the starch formed during assimilation is derived from glucose. He believes that starch is only formed when the solution of glucose reaches a certain strength, different for different species of plants.

J. M. H. M.

Solution of Starch in Leaves. By L. Brasse (*Ann. Agronom.*, **12**, 200—203).—A diastatic ferment can be extracted from green leaves in the following way: The leaves are bruised in a mortar and covered with cold water; after 24 hours they are pressed, and $1\frac{1}{2}$ volumes of 90° alcohol added to the juice, which is then filtered. The same quantity of alcohol is again added to the filtrate, and after a few minutes the clear liquid is syphoned off, and the precipitate thrown on a filter, and rapidly washed once or twice with alcohol of 65° G. L. The diastase is obtained in solution by dissolving the washed precipitate in water, and filtering. 10 c.c. of such a solution is added to 0·5 gram of starch made into paste, and kept at 63°, and the formation of sugar is shown by comparison with a similar flask to which a few drops of chloroform have been added. The leaves of the potato, dahlia, artichoke, maize, beet, castor-oil plant, and the unripe seeds of the opium poppy, sunflower, and castor-oil plant, have all yielded positive results. Microbes have not been found in the solution, and the starch was in all cases transformed into a mixture of reducing sugar and dextrin. To connect this with the formation of sugar in the growing plant, the author shows by a series of experiments that although diastase will only act on *starch-paste* and not on crude starch at 60°, 57°, and 50°, yet at 42° and at 34° it always transforms a little crude starch into sugar. The quantity of sugar produced reaches a limit in 24 or 36 hours; but if it be dialysed out of the solution as fast as it is formed, the formation is rendered continuous. The same result is produced by diluting the solution, so that it seems to be the accumulation of sugar which puts an end to the diastatic action. Cuboni's experiment, therefore (Abstr., 1885, 1004), in which the disappearance of starch from a vine leaf placed in the dark was prevented by an annular incision in the stem above and below the leaf, does not negative the idea that starch is transformed into sugar by a diastatic ferment in the leaf; arrest of sugar formation would under these circumstances be brought about by accumulation of sugar in the isolated leaf.

J. M. H. M.

Proteïd Substance in Latex. By J. R. Green (*Proc. Roy. Soc.*, **40**, 28—39).—Martin has recently described four proteïds present in the dried milk of the fruit of the papaw plant, namely, two belonging to the group of albuminoses, a globulin and an albumin (this vol., pp. 641—642). In the latex of several caoutchouc-yielding plants of the natural orders *Apocyneæ* and *Sapotaceæ*, the author has found a dialysable proteïd resembling peptone, an albumose and an albumin; in the latex of the manihot (*Euphorbiaceæ*) a globulin, and in the common lettuce (*Compositæ*) a hemialbumose. Of these, the albumin and globulin are probably identical with those described by Martin, and the former probably identical with Boussingault's vegetable fibrin. The hemialbumose resembles the substance found by Martin, but differs from it in not giving the biuret reaction; it also resembles a substance found by Vines in seeds. The dialysable proteïd is soluble in water, not coagulated on boiling, precipitated by alcohol, carbonic anhydride, and solid magnesium sulphate from saturated neutral or acid solutions. It does not give the biuret reaction; is converted into true peptone by the action of pepsin. The albumose from *Mimusops* is soluble in distilled water, not coagulated by boiling, precipitated slowly by nitric acid at about 70°, but not precipitated by acetic acid and potassium ferrocyanide. V. H. V.

Composition of Bokhara Clover (Melilotus leucantha). By J. M. H. Munro (*Field*, April 3, 1886).—The plants from which the samples were cut, were about 5 feet high, and in full flower; the flowering branches and the upper portions of the leafy branches were selected for analysis:—

	Fresh plant.		Dry matter.	
Water	79·18		—	
Ash	1·66		7·96	
Light petroleum extract (essential oil, fatty oil, and altered chlorophyll)	0·43		2·07	
Ether extract (chlorophyll and resin)	0·35		1·70	
Absolute alcohol extract	2·82		13·55	
*True albuminoïds	2·85		13·67	
Digestible cellulose	5·53		26·58	
Lignin and incrusting substances	0·22	crude fibre, 5·50	1·07	crude fibre, 26·42
Indigestible cellulose	5·28		25·35	
Sugar, dextrin, and other soluble carbohydrates; amides, nitrates, and other non-albuminoïd nitrogenous substances†	1·68		8·05	
	100·00		100·00	
Total nitrogen	0·56		2·71	
*Albuminoïd nitrogen	0·45		2·19	
†Non-albuminoïd nitrogen	0·11		0·52	

The three extracts mentioned in the analysis were prepared by using the solvents in succession; the light petroleum extract deposited crystals, probably of coumarin. J. M. H. M.

Composition of Goat's Rue (Galega officinalis). By J. M. H. Munro (*Field*, March 20, 1886).—This leguminous plant has been recently recommended as a forage crop. A sample, cut in full flower, was analysed with the following result:—

	Dry matter.		Fresh plant.	
Water	—		72·48	
Ash insoluble in water	7·09	9·19	1·95	2·53
„ containing sand 0·48				
„ „ calcium carbonate. 4·97				
„ „ „ phosphate 0·86				
Ash soluble in water	2·10		0·58	
„ containing potash (K_2O) 0·70				
Light petroleum extract (oil and altered chlorophyll)	2·02		0·56	
Ether extract (resin and chlorophyll)	3·43		0·94	
Absolute alcohol extract	10·94		3·01	
True albuminoïds	11·94		3·28	
Digestible fibre	12·78		3·52	
Lignin and incrusting substances	3·76	crude fibre, 17·65	1·03	4·85
Indigestible cellulose	13·89		3·82	
Starch, mucilage, dextrin, sugar, vegetable acids, gum, non-albuminoïd* nitrogenous substances, &c.	32·05		8·82	
	100·00		100·00	
Total nitrogen	2·42		0·666	
Albuminoïd nitrogen	1·91		0·526	
*Non-albuminoïd nitrogen	0·51		0·140	

Treated with various solvents in succession, the dried rue yielded the following percentages of extracts:—Light petroleum, 2·02; ether, 3·43; absolute alcohol, 10·94; water, 21·56; sodium hydroxide, of 0·1 per cent., followed by hydrochloric acid of 1 per cent., 30·43: undissolved, including digestible cellulose and woody fibre, 31·62: 100·00. J. M. H. M.

The Soja Bean. By J. Stingl and T. Morawski (*Monatsh. Chem.*, **7**, 176—190).—A very active diastatic ferment is present in the soja bean; this when acting on starch converts about two-thirds of it into sugar, about one-third into dextrin.

The soja bean contains only a very small quantity of dextrin; the extractive substance mistaken for dextrin consists of a mixture of sugars. These occur to the extent of about 12 per cent.

A. J. G.

Cholesterin in Vegetable Fats. By E. Heckel and F. Schlagdenhauffen (*Compt. rend.*, **102**, 1317—1319).—The authors have isolated cholesterin from the oil from the seeds of *Gynocardia odorata*, *Giulandina Bonducella*, *Cæsalpinia Bonducella*, and *Abrus precatorius*, and from the mixture of fat and wax obtained from the leaves of

Erythroxylum hypericifolium. The substance was treated with boiling alcohol, and the alcoholic solution after remaining for about a month deposited foliated crystals, melting at 134—138°. In another series of experiments the fatty substances were saponified, and then extracted with a large quantity of ether. The ethereal solution when evaporated, left a residue consisting of rhombohedral tables or slender needles, melting at 135—138°. In both series the crystals gave a red coloration with sulphuric acid and chloroform, or with sulphuric acid, chloroform and ferric chloride. C. H. B.

Cholesterin in the Carrot. By A. Arnaud (*Compt. rend.*, **102**, 1319—1322).—The light petroleum used in the preparation of carrotene (this vol., p. 711), is distilled off, and leaves a buttery residue of impure vegetable cholesterin. This residue is dissolved in boiling alcohol, filtered, and the cholesterin which separates on cooling is purified by repeated recrystallisation from alcohol. In order to obtain a perfectly pure product, a quantity was subjected to repeated treatment with alcohol until its solubility and melting point remained constant. The cholesterin thus obtained has the composition $C_{26}H_{44}O$, melts at 136·5°, is insoluble in water, slightly soluble in cold alcohol, readily soluble in boiling alcohol and in ether, carbon bisulphide, chloroform, light petroleum, and oils, from which it crystallises in anhydrous needles. It is not saponifiable, and is not affected by dilute acids. It is lævogyrate, the rotatory power of a chloroform solution being $[\alpha]_D = -35°$.

Husemann's hydrocarrotine was simply impure cholesterin.

C. H. B.

Absorption of Potash and Lime from the Soil by Beetroot during the first year of Vegetation. By H. Leplay (*Compt. rend.*, **102**, 1254—1257; see also Abstr., 1883, 235, 368).—The experiments described in this paper were undertaken mainly in reply to a criticism of the author's former papers by Berthelot and André (*Compt. rend.*, 1884). Beetroots were sown in sand which had been strongly heated in order to remove all organic matter, and were watered with distilled water containing per litre, 0·1 gram potassium hydrogen carbonate, 0·1 gram ammonium hydrogen carbonate, 100 c.c. of a saturated solution of carbonic anhydride, and 100 c.c. of a saturated solution of calcium sulphate. The beetroots were analysed at various stages with the following results, the proportions of potash and lime being given in Gay-Lussac's alkalimetrical degrees, and the quantities being the total amount present in 100 beetroots.

	1.	2.	3.
Solid matter	1·953 grams	8·263 grams	20·670 grams
Potash.....	0·599°	15·454°	24·180°
Lime	0·829°	16·363°	16·302°

	4.	5.	6.
Solid matter....	51·670 grams	72·345 grams	70·392 grams
Potash	44·149°	68·329°	67·730°
Lime..... ..	69·748°	86·050°	85·221°

(1) Before sowing; (2) roots and leaves after 36 days; (3) roots after 150 days; (4) leaves after 150 days; (5) roots and leaves after 150 days; (6) increase during vegetation.

These results show that for 1 kilo. of root there were formed 2·71 kilos. of leaves, which absorbed from the soil during 150 days—

Potash, in the roots, 5·947 grams; in the leaves, 10·824 grams.

Lime, in the roots, 2·405 grams; in the leaves, 10·211 grams.

The potassium and calcium existing in the soil as hydrogen carbonates are absorbed by the roots of the beet, and are afterwards found in the leaves and root in combination with organic acids formed by the reduction of the carbonic acid. C. H. B.

Ammonia in Soils. By T. Schloesing (*Compt. rend.*, **102**, 1217—1221 and 1357—1361).—The first paper is mainly a rejoinder to Berthelot and André (this vol., p. 740). The object in rapidly drying a soil before analysis is to arrest the action of microbes and thus prevent any alteration in the nitrogenous organic matter, for the estimation of this organic matter is the chief end of the analysis, and the estimation of the ammonia existing as such in the soil is of little practical value, since its quantity is always varying.

In the second paper the author shows that when vegetable soils are mixed with solutions of sodium or calcium hydroxide, there is a continual evolution of ammonia resulting from the action of the alkali on the nitrogenous organic matter in the soil. Three different solutions of soda were used, I containing 20 grams per litre, II containing 50 grams, and III 100 grams. Two samples of soil were mixed with these solutions and allowed to stand for 48 hours at the ordinary temperature, the evolved ammonia being absorbed in standard acid. The quantity of ammonia in the soils was also estimated by Boussingault's method of boiling with magnesia.

	Ammonia per kilo.	
	Soil from Boulogne.	Soil from Neauphle.
Soda solution, I....	11·3 mgrms.	34·4 mgrms.
„ II....	40·5 „	61·6 „
„ III....	75·7 „	96·0 „
Boussingault's method	8·1 „	9·0 „

	Ammonia per kilo.			
	Soil from Boulogne.		Soil from Neauphle.	
	With milk of lime.	With conc. soda solution.	With milk of lime.	With conc. soda solution.
First two days.....	21·6 mgrms.	129·4 mgrms.	22·0 mgrms.	101·0 mgrms.
Two following days.....	21·7 „	31·9 „	12·8 „	24·2 „
Three „	16·1 „	21·7 „	7·5 „	11·9 „
Six „	22·4 „	30·7 „	12·3 „	24·9 „

It is evident that the quantity of ammonia evolved increases with the strength of the alkaline solution. The preceding results also show that this production of ammonia continues for several days.

These experiments, as well as others made with weaker soda solution, show conclusively that the evolution of ammonia has not ceased at the end of 48 hours as Berthelot and André supposed.

C. H. B.

Ammonia in Soils. By Berthelot and André (*Compt. rend.*, **102**, 1286—1290).—A continuation of the discussion with Schloesing.

Influence of Superphosphates on the Production of Sugar. By A. Nantier (*Ann. Agronom.*, **12**, 119—127).—The author's experiments were designed to prove that no benefit is derived from the indiscriminate and excessive use of phosphatic manures on all soils employed for growing sugar beet. The first series was carried out on a soil rich in phosphoric acid, as well as in potash and nitrogen, containing 0·34 per cent. P_2O_5; 0·528 per cent. K_2O; and 0·170 per cent. N. It had received a dressing of 30,000 kilos. per hectare of farmyard manure in the previous autumn. Eleven plots were marked out, each 1 are in area. One of them did not receive any manure; three received 75 kilos. nitrogen per hectare in the respective forms of sodium nitrate, ammonium sulphate, and oil-cake; three more received the same nitrogenous manures, with the addition of 75 kilos. per hectare of phosphoric acid soluble in water; and a third set of three plots received again the same quantities of nitrogen, with 150 kilos. per hectare of soluble phosphoric acid. The eleventh plot received a dressing of phosphoguano, containing 75 kilos. per hectare of organic nitrogen, and 75 kilos. per hectare soluble phosphoric acid. Although the total weight of crop was increased on nearly all the plots receiving sodium nitrate and ammonium sulphate, the density of the beet juice and its richness in sugar were in nearly every case lower on the manured plots than on the unmanured. By valuing the produce at 32 fr. per 1000 kilos. with the density of juice at 7°, and deducting 1 fr. from the price for every $\frac{1}{10}$° of diminution in density, it appears that only in one plot out of the ten (75 kilos. N as sodium nitrate alone) did the increase in value of the crop defray the cost of the manure. The phosphatic manures were in fact absolutely without effect. A second series of trials was conducted on much poorer land, containing only 0·080 per cent. of P_2O_5, with 0·170 per cent. N, and 0·423 per cent. K_2O. In this case, although 75 kilos. phosphoric acid (as superphosphate) produced no increase of crop, the density of the juice was raised from 7·3° to 7·9°, and the sugar per decilitre from 14·91 grams to 15·88 grams, representing a net gain in value of about 64 fr. per hectare. 75 kilos. phosphoric acid in the form of ground mineral phosphate produced almost exactly the same result at less expense, and three times that quantity of mineral phosphate, namely, 225 kilos. P_2O_5 per acre, costing the same as the 75 kilos. P_2O_5 in superphosphate, produced no better result.

J. M. H. M.

Analytical Chemistry.

Estimation of Chlorine, Bromine, Iodine, Cyanogen, Ferrocyanogen, and Ferricyanogen, by Field's Method. By C. Willgerodt (*Chem. Zeit.*, **10**, 637—638; 665—666).—A modification of Field's method (this Journal, 1857, 234) is employed, in which the mixture of silver salts is converted into silver bromide or iodide by digesting and stirring whilst hot with large excess of potassium bromide or iodide for $\frac{1}{4}$ to $\frac{1}{2}$ an hour. The results obtained show that in this way these acid radicles may be quantitatively and satisfactorily determined in the presence of all or some of the following acids or their salts:—Hydrobromic, hydrochloric, hydriodic, hydroferro- and hydroferri-cyanic. The fact that silver iodide is neither decomposed nor dissolved by digesting with potassium bromide is confirmed. Results with potassium cyanide were not satisfactory, owing probably to the impurities in the cyanide. Details of methods and calculations are given. D. A. L.

Detection of Bromides. By H. J. H. Fenton (*Chem. News*, **53**, 193—194).—Sodium carbamate is immediately decomposed by sodium hypobromite but not by hypochlorite (this vol., p. 501). Therefore when sodium bromide is added to a solution containing sodium carbamate, hypochlorite and hydroxide, nitrogen is evolved; this is shown to be due to the intermediate formation of hypobromite, hence a small quantity of bromide will decompose a large quantity of carbamate. The initial rate of the action is more rapid the greater the mass of the bromide, although the final result is the same with both weak and strong solutions. This reaction forms a delicate test for bromine in presence of unlimited quantities of chlorides, hypochlorites, &c.:—for this purpose two equal quantities of the test mixture are shaken, one with the suspected liquid, one with an equal volume of distilled water; after resting some time, if bromine is present, gas will be seen coming off in the one and not in the other, or at least not to the same extent. In this way it is easy to detect one part of bromine in 6000 of water. Iodides give a slight action, probably due to traces of bromide as impurity. Sodium carbamate may be prepared by dissolving ammonium carbamate in a strong solution of sodium hydroxide, and allowing the mixture to stand over sulphuric acid under a bell-jar, or by treating ammonium carbamate with a mixture of sodium hypochlorite and hydroxide.

D. A. L.

Error in the Nitrometric Analysis of Sulphuric Acid. By T. Bayley (*Chem. News*, **53**, 266—267).—The author has always taken precautions against the error suggested by Lunge (this vol., p. 391). He now, on experimental evidence, attributes the retention of nitric oxide by the sulphuric acid to the presence of iron.

D. A. L.

Determination of the Nitrogen in Nitrates by Kjeldahl's Method. By M. JODLBAUER (*Chem. Centr.*, 1886, 433—434).—In presence of various organic matters a greater or smaller proportion of the nitrogen of a nitrate is converted into ammonia by heating with sulphuric acid. By the following treatment the results show quantitative accuracy. Half a gram of potassium nitrate is treated with 20 c.c. of concentrated sulphuric acid and 2·5 c.c. of phenolsulphonic acid. The latter is prepared by dissolving 50 grams of phenol in sulphuric acid to 100 c.c. A few grams of zinc powder and 5 drops of a solution of platinic chloride containing 0·04 gram of platinum per c.c. are then added; the mixture is heated for four hours, and the operation completed as in Kjeldahl's ordinary process. By the addition of phosphoric anhydride the time of heating may be shortened to two hours. M. J. S.

Testing Nitric Acid and Sodium Nitrate for Iodine and Iodic Acid. By H. BECKURTS and W. ROUGEMONT (*Chem. Centr.*, 1886, 445).—The authors endorse Hager's suggestion to employ the reaction between an iodide and an iodate in presence of acid, which they find furnishes a far more sensitive test than the reduction with tin and agitation with chloroform prescribed by the German Pharmacopœia. The nitric acid is heated to boiling, which expels oxides of nitrogen and oxidises any iodine to iodic acid; it is then diluted with 5 vols. of boiled water, and a few drops of a solution of potassium iodide and starch in boiled water are added. Sodium nitrate is dissolved to a 5 per cent. solution in boiled water, acidified with nitric acid, and similarly tested. With some specimens of saltpetre a violet colour was obtained, which was perhaps due to the presence of traces of chlorates or bromates. M. J. S.

Precipitation of Phosphoric Acid as Ammonium Magnesium Phosphate in Presence of Ammonium Citrate. By C. MOHR (*Chem. Zeit.*, **10**, 675).—It is proved experimentally that when phosphoric acid is precipitated from solution as ammonium magnesium phosphate in the presence of ammonium citrate, or ammonium citrate and iron chloride, or ammonium citrate and calcium chloride, lower results are obtained than when no such admixtures are present. The deficiency is greatest in the first case—especially when large quantities of ammonium citrate are used; not so great in the second, and least in the third; the Joulie-Millot alkaline solution of magnesium citrate gives rise to very low results. On the other hand, alkaline ammonium citrate is the best solvent for "retrograde" and dibasic phosphate; therefore to minimise errors the following method of procedure is recommended:—Extract the superphosphate with warm—not hot—water, adding a sufficient quantity of sodium acetate. Determine the soluble phosphate in the solution, and digest the residue with alkaline ammonium citrate for one hour at 40—50°; then precipitate the filtered solution with magnesia mixture for "retrograde" phosphate. Available phosphoric acid is the sum of the two. Temperature plays an important part in these determinations of retrograde phosphate; for example, two portions of the same sample were treated

in a similar manner, but one was digested with citrate for one hour at the ordinary temperature and gave 0·998 per cent. P_2O_5, the other was digested for same period of time at 45—50°, and gave 2·572 per cent. (compare Abstr., 1885, 688 and 931). D. A. L.

Simplification of the Molybdate Method for Determining Phosphorus. By M. A. v. Reis (*Chem. Centr.*, 1886, 437).—Solutions of molybdic acid reduced by zinc can be titrated with permanganate: 0·8381 gram of MoO_3 has the same reducing power as 1 gram of oxalic acid.

Ammonium phosphomolybdate, precipitated from a hot solution of a pig-iron containing more than 1 per cent. of phosphorus, has the composition $NH_4PO_4,11MoO_3$ (*sic*) if allowed to deposit at ordinary temperatures. Steel solutions must be kept for an hour at 80—90° to obtain the same precipitate. When little or no iron is present an excess of molybdic acid separates.

The solution of the iron in nitric acid is freed if necessary from silica, and is then mixed with a large quantity of ammonium nitrate and precipitated hot with ammonium molybdate. After three hours' repose (besides half an hour at 80—90° in the case of steel) the precipitate is filtered off and washed with a 15 per cent. molybdate solution. The precipitate is dissolved in ammonia; the solution is moderately acidified with sulphuric acid, warmed, and reduced by zinc. After an hour the greenish-brown liquid is poured off the undissolved zinc and titrated with permanganate until a permanent rose colour is obtained. A greenish tint towards the end of the titration indicates that more acid is required. M. J. S.

Estimation of Phosphoric Acid in Thomas-Process Slag. By J. Klein (*Chem. Zeit.*, **10**, 721).—The slag is decomposed by boiling vigorously with concentrated hydrochloric acid for an hour or an hour and a half. By this means the iron phosphide is not attacked, and the results obtained compare well with those obtained by other methods. Iron phosphide was only observed in two samples out of seven analysed; it would hence appear not to be so prevalent in these slags as is generally supposed. D. A. L.

Estimation of Silicon in Iron. By L. Blum (*Chem. Zeit.*, **10**, 702—703).—The author's method, already described (*ibid.*, **9**, 1373), is compared with the old nitric acid method and with the potassium chlorate method. The chlorate method gives uniformly low results; this is attributed to the formation and volatilisation of silicon chloride or hydrochloride; in his process the corresponding bromine compounds are formed; but these, being less stable than the chlorine compounds, decompose, and hence do not volatilise and cause loss of silicon. The author's method is also the most convenient.

D. A. L.

New Apparatus for the Estimation of Carbonic Anhydride in the Air. By T. C. Van Nüys (*Amer. Chem. J.*, **8**, 190—196).—The apparatus consists of a stoppered globe holding some 6 litres; through the stopper pure water may be passed for washing all barium

hydroxide solution out of the globe. The lower portion of the globe is a narrow tube provided with a glass stopcock; it is connected by a rubber tube with a half litre flask, through the cork of which pass the end of a tube containing solid sodium hydroxide and the end of a burette holding standard oxalic acid; before each titration this flask is filled with air free from carbonic anhydride. The globe having been filled with the air under examination at ascertained temperature and pressure, the measured excess of baryta water is introduced and spread over the inside of the globe; two hours is allowed for the absorption. The contents of the globe are then run into the titration flask and the globe washed and the liquids titrated—rosolic acid being used as indicator. The water used for washing the globe and filling the connecting tubes so as to displace all ordinary air, must have been well boiled. The principal source of error is the determination of the temperature of the air at the time of filling the globe. H. B.

New Method for the Estimation of Zinc. By G. Lösekann and T. Meyer (*Chem. Zeit.*, **10**, 729—730).—The solution of zinc chloride or sulphate is treated with excess of ammonia and disodium hydrogen phosphate and neutralised with hydrochloric or sulphuric acid, when zinc ammonium phosphate is precipitated. The whole is heated to boiling, and after a few hours filtered. The precipitate is washed with hot water, dried, ignited until constant in weight; on cooling the fused zinc pyrophosphate has a tendency to burst suddenly into fine powder, weighings should therefore be conducted in a covered crucible. The amount of zinc in solution should not exceed 0·3 gram, nor the quantity of disodium phosphate employed be more than 50 c.c. of a 1 to 10 solution. This method is applicable in presence of magnesium in sulphuric acid solution, but not when manganese is present. D. A. L.

Reduction of Ferric Solutions by Means of Amalgamated Zinc and Platinum Foil. By A. L. Beebe (*Chem. News*, **53**, 269).—In the suggested modification of the usual method of working this process, the amalgamated zinc is supported in the solution in a piece of perforated platinum foil bent into a convenient form and suspended from a piece of stout wire, another piece of platinum foil is immersed in the solution in contact with the stout wire, but not touching the zinc. By this means, the amalgamation of the platinum is prevented, and the reduction proceeds without interruption; when it is complete, the zinc is easily removed, and the chance of its projection into the titrating vessel avoided. D. A. L.

Estimation of Nickel on Nickeled Iron. By A. Köbrich (*Chem. Zeit.*, **10**, 747).—The nickel is dissolved off the iron by means of 1·180 nitric acid diluted with an equal volume of water. Hydrochloric acid is added to the solution which is warmed until all the iron has become oxidised to the ferric state; it is then treated with excess of ammonia and ammonium chloride, and digested. The iron hydroxide is collected and the digestion with ammonia and ammonium chloride repeated until all the nickel is in solution. The nickel is precipitated as sulphide, redissolved, reprecipitated as oxide and reduced with hydrogen. D. A. L.

General and Physical Chemistry.

Refraction of Carbonic Anhydride and Cyanogen. By J. Chappuis and C. Rivière (*Compt. rend.*, **103**, 37—39).—Experiments on carbonic anhydride at 21°, and under pressures up to 19 atmos., show that the relation between the refractive index for D and the pressure may be expressed by the formula

$$n - 1 = 0{\cdot}000540p(1 + 0{\cdot}0076p + 0{\cdot}0000050p),$$

and the function $\frac{n^2-1}{n^2+1}$ is represented between the same limits by the equation—

$$\frac{n^2 - 1}{n^2 + 2} = 0{\cdot}000360p(1 + 0{\cdot}0075p + 0{\cdot}0000049p^2).$$

The refractive index at 0° under a pressure of 760 mm. is 1·000448. Previous determinations have given 1·000454 (Mascart), and 1·000449 (Dulong). The laws $\frac{n-1}{d}$ = const., and $\frac{n^2-1}{(n^2+2)d}$ = const., hold good for carbonic anhydride between the given limits.

The refraction of cyanogen at various temperatures and pressures up to 3 metres is represented by the equation—

$$n-1 = ap(1 + bp),$$

the values of a and b at different temperatures being given in the following table:—

	a.	b.
0°	0·001049	0·0459
7	0·001036	0·0370
9·5	0·001022	0·0377
14	0·001007	0·0364
17	0·000991	0·0360
25	0·000971	0·0312
35	0·000946	0·0263

The index at 0° and 760 mm. is 1·000825. C. H. B.

Spectra of Didymium and Samarium. By E. Demarçay (*Compt. rend.*, **102**, 1551—1552).—Examination of the products of the fractionation of didymium and samarium shows that the samarium bands 4170 and 3740 can be distinctly separated from the bands 4070 and 4000. It follows that the samarium giving these four bands really contains two substances. The author retains the name samarium for the substance giving the bands 4070 and 4000, and denotes the other substance by S_1.

The spectrum of didymium contains a narrow band at about 4340

which does not belong to Welsbach's praseo-didymium or neo-didymium, and may possibly be due to a third substance.

C. H. B.

Fluorescence Spectrum of Yttrium. By L. DE BOISBAUDRAN (*Compt. rend.*, **102**, 1536—1539).—A sample of terbia giving a reversal spectrum which contained all the bands in the spectrum $Z\beta$, with only an indication of the yellow band of $Z\alpha$, was mixed with some purified yttria, which gave no fluorescence spectrum, or only a trace of the citron band. The anhydrous sulphate of this mixture gave a brilliant fluorescence spectrum, in which were the two green bands formerly ascribed by Crookes to yttria. The reversal spectrum of the terbia showed only a single green band. In this experiment, the samarium spectrum was distinct, but the spectrum $Z\beta$ was feeble.

A small quantity of the same terbia was also mixed with lime. The mixture gave a brilliant fluorescence spectrum, in which the green band was single, whilst the other bands of $Z\beta$ were well marked, and the fluorescence spectrum $Z\alpha$ was also well developed. The two bands described by Crookes were not visible, and the samarium bands were feeble.

Similar experiments were made with an earth giving a strong reversal spectrum of $Z\alpha$ and a feeble spectrum of $Z\beta$. The mixture with yttria gave the citron band described by Crookes, the green band being weaker and double. The mixture with lime gave the yellow and blue bands of $Z\alpha$ brilliantly, whilst the green band was single.

It would seem that the double green band and the citron band described by Crookes are the author's reversal bands $Z\alpha$ and $Z\beta$, modified by the nature of the solid substance with which the substance giving these bands is mixed. It is possible that the two sets of bands have a different origin, but in this case it would follow that Crookes's bands are produced to the exclusion of $Z\alpha$ and $Z\beta$ in presence of yttria, whilst in presence of lime the reverse is the case.

C. H. B.

Absorption-spectra of Chromic Acid and Alkaline Chromates. By P. SABATIER (*Compt. rend.*, **103**, 49—52).—By means of a modified Crova's spectro-photometer the author has determined the coefficients of absorption of chromic acid and of the alkaline chromates. The values of α for different wave-lengths were not sensibly affected by the thickness of the layer of liquid through which the light passed, and this result is an important confirmation of the law of thicknesses. The values obtained were as follows:—

	Coefficient of transmission.		
Wave-length.	1.	2.	3.
5450	—	0·005	0·005
5480	0·02	0·03	0·024
5550	0·137	0·15	0·143
5620	0·34	0·352	0·36
5690	0·623	0·63	0·631
5770	0·815	0·82	—
5850	0·905	0·894	—
5930	0·945	0·955	—

Beyond wave-length 5450 the coefficients become practically *nil*; in very dilute solutions, the coefficient for wave-length 5180 is about 0·000013. The values are the same for the acid as for the salts, for solid potassium dichromate as for its solution, for the ammoniacal salt as for the potassium salt, and it follows that the absorption exerted by solid or dissolved alkaline dichromates is sensibly identical with that of the chromic acid which they contain.

With normal potassium chromate the following results were obtained, α_1 being the values for a solution containing 1 equivalent of salt per litre, and α_2 for a solution containing 2 equivalents.

λ	4940	4990	5030	5060	5080	5110	5130	5180	5240
α_1	—	0·06	0·18	0·325	0·44	0·61	0·69	0·85	0·92
α_2	0·025	0·108	0·207	0·43	0·51	0·62	0·69	0·84	0·93

The absorption is slightly greater in the more dilute solution, and this points to slight dissociation with formation of some dichromate, which, however, is only produced in very minute quantity.

C. H. B.

Galvanic Polarisation. By H. Jahn (*Ann. Phys. Chem.* [2], **28**, 498—508).—Determinations were made of the electromotive force of polarisation of solutions of various salts. The apparatus used consisted of a tuning-fork contact breaker, by which the solutions were alternately polarised by a battery of three Bunsens, and circuited through a tangent galvanometer, the latter being compared with a Clark's cell. The polarisation cell was placed in melting ice.

The values obtained were compared with the E.M.F.'s produced by elements formed of different pairs of the salts experimented with, thus: $p_{ZnSO_4} - p_{CuSO_4} = E$: the results compared very favourably.

From these values, the secondary heat evolution, as distinct from that due to resistance, is determined from the equation $W_s = aJpt - Q$, where W_s = secondary heat, a = heat equivalent of unit of work, J = strength of current, p = polarisation E.M.F., and Q = heat of combination. The results agree closely with those obtained by Favre by direct experiment. It is remarkable that they are all multiples of the same number: thus copper, zinc, and cadmium salts = 2 × 10 cal.; lead salts = 3 × 10 cal.; silver salts and sulphuric acid = 4 × 10 cal.

Lastly, the polarisation E.M.F. of the same salts for a temperature of 34° were determined. For zinc or copper salts, the polarisation E.M.F.'s are in much the same relation as at 0°, hence the E.M.F. of a Daniell's element must, in accordance with Helmholtz's laws, be independent of temperature.

H. K. T.

Electrical Conductivity of Mixtures of Salts. By E. Bouty (*Compt. rend.*, **103**, 39—42).—In dilute solutions, the conductivity of mixtures of salts of the same acid or the same base, which have no known chemical action on one another, is sensibly equal to the sum of the conductivities of its constituents.

When 2 molecules of simple salts are replaced by 1 molecule of a double salt, the resistance is increased. Experiments with zinc and potassium sulphates show that in dilute solutions the quantity of

double salt formed is only very small, but is still distinctly recognisable in solutions in which $m = 0{\cdot}1$.

The resistance of a solution containing two different acids and two different bases affords a measure of the distribution of the acids and bases. Measurements with a solution containing zinc and potassium, nitric and sulphuric acids, show that the proportion of the group $Zn(NO_3)_2 + K_2SO_4$ is equal to 0·276, and in more dilute solutions ($m = 0{\cdot}1$) 0·263. An excess of potassium sulphate or zinc nitrate does not sensibly affect this value, but as the dilution of the solution increases, the coefficients in the equation approach more closely to unity, and ultimately the measurements become illusory.

C. H. B.

Equivalence of Chemical Energy and Current Energy. By H. Jahn (*Ann. Phys. Chem.* [2], **28**, 491—497).—This is a continuation of the author's experiments (*Ann. Phys. Chem.*, **28**, 21), in which he proves Helmholtz's relation between the secondary heat of a galvanic element and its temperature coefficient.

The elements examined were silver in silver nitrate, with lead in lead nitrate, and copper in copper nitrate respectively. The solutions had a strength of $(M')_2(NO_3)_2 + 100H_2O$.

The chemical heat of the cell is obtained from the formula $Q = W - aJ(\Delta - Jg)t$, where W is the heat evolved in cell, a, the heat equivalent of unit of work, J, the current intensity in ampères, $\Delta - Jg$, the potential difference of poles, and t, the duration of the experiment. The values obtained from this formula agree closely with those obtained from thermochemical data.

The chemical heat less the current heat gives the secondary heat, which is compared with that obtained by calculation from Helmholtz's relation. The following are the results:—

Element.		E.M.F.	Chemical heat.	Current heat.	Secondary heat found.	Secondary heat calculated.
$Ag_2,Ag_2(NO_3)_2$	$Pb(NO_3)_2,Pb$	0·932	50·87	42·98	7·95	7·89
$Ag_2,Ag_2(NO_3)_2$	$Cu(NO_3)_2,Cu$	0·458	30·04	21·12	8·92	8·92

H. K. T.

Heat of Transformation of Vitreous Selenium into Metallic Selenium. By C. Fabre (*Compt. rend.*, **103**, 53—55).—The heat of transformation was measured directly in the calorimeter, and also by the action of bromine-water on the two varieties. The first method gave + 5·46, and the second + 5·76, or a mean value for Se = 78·8 of + 5·61 cal.

Selenium precipitated from alkaline selenides by the action of the air has the same specific gravity and thermal properties as metallic selenium.

C. H. B.

Selenides of the Alkaline Earths. By C. Fabre (*Compt. rend.*, **102**, 1469—1471).—The selenides of calcium, strontium, and barium can be obtained in a state of purity by heating the corresponding selenates at a dull red heat in a current of hydrogen. Care must be taken not to raise the temperature too high, nor to use too large a

quantity of the selenate, otherwise the mass frits and attacks the glass. The selenides are white compounds, which alter rapidly when exposed to air, and become red. They are only slightly soluble in water, and do not phosphoresce like the sulphides. The heats of formation of the selenides were determined by dissolving them in dilute hydrochloric acid. The following results were obtained :—

Ca + Se solid	= CaSe, anhydrous,	develops	+ 78·0	cal.
Sr + Se „	= SrSe „	„	+ 87·16	„
Ba + Se „	= BaSe „	„	+ (z − 108·70)	cal.

z being the heat of formation of barium chloride from its elements.

CaO solid + SeH_2 gas	= CaSe + H_2O	develops	+ 9·76	cal.
SrO „ + SeH_2 „	= SrSe + H_2O	„	+ 20·58	„
BaO „ + SeH_2 „	= BaSe + H_2O	„	+ 20·26	„

These numbers do not differ greatly from the heats of formation of the corresponding sulphides (Sabatier, Abstr., 1881, 492).

C. H. B.

Heat of Formation of the Picrates. By Tscheltzoff (*Ann. Chim. Phys.* [6], **7**, 233—252).—The results which the author has obtained are subjoined in a tabular form :—

Picrate of	Mols. of H_2O of crystallisation.	Heat of solution of		Heat of hydration of the anhydrous salt.	Heat of neutralisation.	Heat of formation.	
		The hydrated salt at 18° to 20°.	The anhydrous salt.			In the solid state.	Total energy calculated from the elements.
		cal.	cal.	cal.	cal.	cal.	cal.
Ca	6	−7·455	+1·080	+ 8·535	+13·783	+ 8·533	+ 95·200
Li	6	−7·214	+0·392	+ 7·606	+13·744	+13·022	+100·500
Ba	6	−7·373	−2·370	+ 5·000	+13·786	+15·616	x + 38·000
Pb	2	−6·579 (?)	−3·530	—	+ 6·913	+ 4·847	+ 44·730
Mg....	8	−7·963	+7·362	+15·315	+14·046	+ 0·969	+ 89·100
Zn	8	−7·947	+5·762	+13·709	+10·243	− 1·189	+ 53·780
Cu	8	−8·822	+1·636	+10·458	+ 7·775	+ 0·469	+ 32·639

From this it appears that the heats of solution of the hydrated picrates containing equal amounts of water of crystallisation are almost identical. The heats of solution of the anhydrous picrates have the same sign as those of the corresponding anhydrous chlorides and nitrates. The heats of neutralisation are almost identical with the values obtained for the neutralisation of nitric and hydrochloric acid with the corresponding bases. In the formation of the anhydrous picrates of magnesium and copper, a very small quantity only of their energy is evolved as heat, and in the case of zinc there is even an absorption of a small amount; from this it is evident that the picrates

of these metals would be more readily acted on by oxidising agents than picrates in whose formation more energy was eliminated from the molecule. The heats of formation of solid anhydrous picrates show that, if the metals were arranged in the order of their affinities for the acid constituent, the order of their affinity for anhydrous picric acid would be quite different from that of the same bases for formic and acetic acids. A. P.

Heat of Combustion of Benzene. By J. Thomsen (*J. pr. Chem.* [2], **33**, 564—567).—This paper is a criticism on the results obtained by Stohmann (this vol., p. 409) for the heat of combustion of benzene. According to the author, the low values obtained result from the length of time taken for the combustion experiment as also the method used, namely, burning the benzene in a miniature lamp within the combustion chamber, whereby great heat is evolved at first, but this gradually diminishes until it reaches *nil*. Finally, the water equivalent of the calorimeter does not seem to have been exactly determined. V. H. V.

Combustion of Benzene: Answer to the Above. By F. Stohmann (*J. pr. Chem.* [2], **33**, 568—576).—It is here shown in answer to the above criticism, firstly, that there is no evidence in the experimental results obtained of any proportionality between the time taken for the combustion of the benzene and the value obtained; secondly, that approximately equal quantities of heat are evolved in equal intervals of time; lastly, the apparatus based on that of Louguinine is fully described, and fairly concordant values given for the water equivalent of the calorimeter. The author also adds some criticisms on the methods used by Thomsen. V. H. V.

Vapour-density Determinations. By V. Meyer (*Ber.*, **19**, 1861—1862).—In the author's well-known vapour-density apparatus, considerable trouble is often experienced when working at high temperatures owing to the cracking of the bulb of the outer glass tube serving as the vapour-bath, so that for temperatures above 300° an iron tube has been employed. The author has, therefore, devised a new vapour-bath in which the liquid is boiled in a cast-iron crucible having a double rim; the annular space so formed contains mercury, into which a long open glass tube dips. In this way the bulb of the vapour-density apparatus is in view, and it is found that the glass mantle is very seldom cracked. A. J. G.

Dissociation of Hydrated Cupric Sulphate. By H. Lescœur (*Comp. rend.*, **102**, 1466—1469).—The following tables show the composition and tension of dissociation of hydrated cupric sulphate at various temperatures:—

At 45°.

Tension of dissociation.	Composition.
58 mm.	$CuSO_4 + 5{\cdot}08\ H_2O$
30 „	$CuSO_4 + 4{\cdot}85\ H_2O$
30 „	$CuSO_4 + 4{\cdot}64\ H_2O$
30 „	$CuSO_4 + 3{\cdot}87\ H_2O$
18 „	$CuSO_4 + 2{\cdot}37\ H_2O$
15 „	$CuSO_4 + 1{\cdot}06\ H_2O$
Less than 1 mm.	$CuSO_4 + 0{\cdot}98\ H_2O$

At 78°.

Tension of dissociation.	Composition.
304 mm.	$CuSO_4 + 5{\cdot}06\ H_2O$
233·5 „	$CuSO_4 + 4{\cdot}13\ H_2O$
238 „	$CuSO_4 + 3{\cdot}71\ H_2O$
233 „	$CuSO_4 + 3{\cdot}41\ H_2O$
142 „	$CuSO_4 + 2{\cdot}61\ H_2O$
145 „	$CuSO_4 + 2{\cdot}10\ H_2O$
148 „	$CuSO_4 + 1{\cdot}79\ H_2O$
Less than 10 mm.	$CuSO_4 + H_2O$

	At 220°.	
Tension of dissociation..	666 mm.	603 mm.
Composition	$CuSO_4 + 0{\cdot}98\ H_2O$.	$CuSO_4 + 0{\cdot}45\ H_2O$.

These results indicate the existence of three hydrates only, namely, $CuSO_4 + 5H_2O$, $CuSO_4 + 3H_2O$, and $CuSO_4 + H_2O$. The author did not obtain the other hydrates stated by various authors to be formed by the gradual dehydration of the pentahydrate. The tensions of dissociation of the three hydrates at different temperatures are as follows:—

$CuSO_4,5H_2O$.

Temp...	10°	15°	20°	25°	30°	35°	40°	60°	80°	100°
Tension.	2·8	4	6	8·5	12·5	17	23	72	263	688 mm.

$CuSO_4,3H_2O$.

Temperature..	30°	35°	40°	60°	80°	100°
Tension.....	5	7·5	11	45	168	525 mm.

$CuSO_4,H_2O$.

Temperature	163°	186·5°	206°	220°
Tension	11	44	143	666 mm.

The crystallised hydrate loses water with great difficulty, but dissociates somewhat better if powdered, the rate of dissociation depending to a certain extent on the degree of subdivision. If heated

in an oven or on a warm plate, the crystals lose their water in a very irregular manner, and yield a product which is not homogeneous; this result is probably due to their low conductivity for heat. These facts probably explain the results obtained by Naumann (this Journal, 1875, 426) and by Muller-Erzbach (Abstr., 1884, 952).

C. H. B.

Decomposition of Ferric Chloride by Water. By G. Fousserau (*Compt. rend.*, **103**, 42—45).—The decomposition of aqueous solutions of ferric chloride was measured by determining the electrical resistance of the liquid. At 100°, decomposition is very rapid, and the resistance diminishes owing to the formation of soluble ferric oxide and hydrochloric acid. With a concentration of 0·001724, the resistance reaches a limit which is 0·365 of the original value. If the liquid which has been heated at 100° is kept for some time at the ordinary temperature, the reverse change takes place, and the resistance increases up to a limit which approximates to that observed with a solution which has not been heated, but has been kept at the ordinary temperature for some time. In the latter case, decomposition is much slower and much less complete than at 100°.

If the variation in resistance were proportional to the amount of change, the relation between the conductivity C and the coefficient of alteration K would be represented by the equation—

$$K = \frac{C - C_0}{C_1 - C_0} = \alpha,$$

C_0 and C_1 being the respective conductivities of the original liquid and the completely altered liquid. This relation, however, is not exact, and the value of K is more accurately represented by expressions of the form—

$$K = \alpha[1 + A(1 - \alpha)],$$

in which A is determined by experiment.

The rate of decomposition is increased by dilution, and the reverse change is accelerated as the concentration increases. Alteration in both directions is more rapid at higher temperatures, and the limit of decomposition increases and becomes sensibly equal to unity at a lower temperature the more dilute the solution. Addition of hydrochloric acid accelerates the change in the reverse direction.

C. H. B.

Size of the Maximum Drops of Ordinary Alcohols and Fatty Acids, and their Aqueous Solutions. By J. Traube (*Ber.*, **19**, 1673—1679).—The drops were observed under the opening of a horizontal tube fused to the capillary of a Poiseuille apparatus; the diameter of the tube was 6 mm. The weight of the drops was then determined from the number contained in the apparatus of known volume, and the specific gravity of the liquid. A table is given containing the results of experiments made with several solutions of alcohols and acids of various strengths.

N. H. M.

Dependence of the Size of Drops on External Influence. By J. Traube (*Ber.*, **19**, 1679—1682).—Experiments made by the

author to determine the influence of curvature of the wall of the tube, and of the rate at which the liquid flows on the size of the drops, led to the same results as those obtained by Guthrie. The material from which the tube is made (for instance, glass or copper) does not appear to influence the size of the drops to any extent.

N. H. M.

Influence of Mass on the Chlorination of Combustible Gases. By A. Römer (*Annalen*, **233**, 172—215).—The author incidentally mentions the fact that dilute sulphuric acid has no action on copper acetylide; on the other hand, strong sulphuric acid completely decomposes the compound without liberating acetylene. The gas obtained by the action of hydrochloric acid on copper acetylide slowly deposits carbon without undergoing any alteration in volume. The residual gas appears to be pure acetylene.

The apparatus used in the experiments on chlorination cannot be explained without the diagrams. The following are the results:—Chlorine has no action in the dark on carbon monoxide, acetylene, ethane, and its homologues, but it combines with the hydrocarbons of the series C_nH_{2n} in the dark. Benzene resembles ethane in its behaviour towards chlorine.

The results of a series of experiments on the action of chlorine on a mixture of combustible gases are given in the following table:—

Proportion of combustible gases.	Chlorine added to 100 vols. of combustible gases.	Relative division of chlorine.	Ratio of constants of affinity.
CH_4.... 100·0 H_2 .... 84·7	27·8	81·6 18·4	$c : c'$ 4·72
CH_4.... 100·0 H_2 .... 108·7	35·5	80·4 19·6	7·68
CH_4.... 100·0 H_2 .... 67·83	47·9	78·64 21·36	3·68
C_3H_8... 100·0 H_2 .... 64·22	All the chlorine combined with the propane.		
C_3H_8... 100·0 H_2 .... 134·9	All the chlorine combined with the propane. The chlorine formed a di-substitution product, in preference to uniting with the hydrogen.		
C_2H_2... 100·0 H_2 .... 110·6	All the chlorine combined with the acetylene.		
H_2 .... 100·0 CO .... 31·54	23·1	95·14 4·86	7·12
H_2 .... 100·0 CO .... 88·7	47·1	75·94 24·06	4·07
H_2 .... 100·0 CO .... 219·05	36·34	57·53 42·47	4·32
C_3H_8... 100·0 C_2H_2... 163·43	33·2	51·19 48·81	3·47
C_3H_8... 100·0 C_2H_2... 56·3	46·23	70·17 29·83	1·47

	Proportion of combustible gases.	Chlorine added to 100 vols. of combustible gases.	Relative division of chlorine.	Ratio of constants of affinity.
C_3H_8 ...	100·0	52·9	62·60	1·99
C_2H_2 ...	94·87		37·40	
C_3H_8 ...	100·0	Only the excess of chlorine unites with the methane.		
CH_4 ...	209·5			

From these numbers it is apparent that the action of the chlorine on the substances under investigation is not proportional to the mass. The law of Guldberg and Waage is not directly applicable to this class of phenomena. W. C. W.

Rudimentary Formula of the Rate of Reactions. By F. Urech (*Ber.*, **19**, 1700—1706).—The author discusses the formulæ of Berthelot and Guldberg and others, and that of Wilheling considered from its theoretical point of view.

Tension of Saturated Vapours over Liquid and Solid Substances. By W. Fischer (*Ann. Phys. Chem.* [2], **28**, 400—432).—In this paper, the author proves experimentally that the tensions of aqueous vapour over ice and water respectively at 0° are not identical, but that the vapour-tension curve of ice lies lower than that of water for corresponding temperatures, the two curves meeting at the melting point.

This result was predicted by Kirchhoff from calculations based on the mechanical function of water in the two cases, (1) in which water at 0° was directly converted into vapour at 0°; (2) in which the water at 0° was first converted into ice at 0°, and then into vapour at 0°. A quotient difference of 0·044 mm. for the two curves was obtained.

The only experimental results extant are those of Regnault, leading to conclusions opposite to those of the author, but they are few in number.

The apparatus used consisted of tubes of the shape of an inverted **L**, the short limb being closed the long one open. The open end was plunged into a beaker of boiling water, and some water previously introduced into the short limb raised to boiling until the air was driven out. This was repeated 10 or 12 times, the water in the beaker being maintained in ebullition the whole time. The open end was then plunged under mercury and the water in the apparatus again boiled out, until only a little remained in the short limb. The apparatus was then allowed to cool, and any water in the long limb driven over into the short one by plunging the latter into ice. Two such tubes were placed in a mercury trough together with a carefully prepared barometer. The water in one of the tubes was frozen, and the short limbs of the tubes maintained at various temperatures, the heights of the mercury in the long limbs being measured by means of a cathetometer. From these data, the author obtains for an interval of − 4° to 10° the equations—

For water: $p = 4{\cdot}628 + 0{\cdot}32535 + 0{\cdot}008705t^2$;

For ice: $p = 4{\cdot}641 + 0{\cdot}37190t + 0{\cdot}011021t^2$.

The vapour-tension of water or ice at 0° = 4·63 mm. (Regnault, 4·60.) Since the vapour-tensions of ice and water at 0° are the same, the latent heat of vaporisation of ice is equal to the sum of the latent heats of vaporisation of water and the latent heat of fusion of ice.

Similar experiments were made with benzene carefully purified and dried, and gave data from which were deduced the equations—

For solid benzene: $p = 24{\cdot}985 + 1{\cdot}6856t + 0{\cdot}031339\ t^2$;

For liquid benzene: $p = 26{\cdot}40 + 1{\cdot}4295t + 0{\cdot}04505t^2$.

The two curves do not meet at the melting point (5·3°), but are 0·44 mm. apart at this point.

The author further determines the specific heat of liquid benzene = $0{\cdot}3102 + 0{\cdot}002168t$; of solid benzene = 0·319; and the latent heat of fusion of benzene = 30·085. From these, together with the latent heat of vaporisation, 107·17 (*Mousson's Physik*), the equation $R = r + q - 1{\cdot}5 = 136{\cdot}7$ cal. at 5·3° is obtained from Clausius' formulæ, where R is the latent heat of vaporisation of solid benzene, r that of liquid benzene, and q the latent heat of fusion of benzene.

H. K. T.

Solution. By W. Alexéeff (*Ann. Phys. Chem.* [2], **28**, 305—338).—In this paper, the author collects together the results of his previous experiments on solution. The solution of a liquid by a liquid is chosen as being the simplest. The experimental method consists in sealing weighed quantities of the two liquids in a tube and gradually heating until they unite to a homogeneous liquid, the temperature of mixing being noted. From a number of such experiments a curve is obtained. The results fall into two classes. First, those obtained from liquids which have no action on one another. Secondly, those obtained with liquids which combine in solution.

Amongst the first are water with aniline, phenol, aniline phenate, and fused benzoic, salicylic and metanitrobenzoic acids, and molten sulphur with benzene, toluene, chlorbenzene, aniline, and oil of mustard. In every case, a gradual rise in temperature was accompanied by a corresponding increase in the quantity of one of the constituents until, at a certain temperature, the two liquids mixed in all proportions.

In the second class are secondary butyl alcohol, isobutyl alcohol, and amyl alcohol with water. All these give curves in which increase of temperature is accompanied by decrease in solubility up to a certain point, this result being due to the gradual dissociation of the hydrate formed at low temperatures. With further rise of temperature the solubility again increases until the two liquids mix in all proportions. In the case of secondary butyl alcohol a maximum exists at 0°, the solubility decreasing with change of temperature in either direction.

In the case of diethylamine and water (comp. Guthrie, Abstr., 1885, 337, 339) the solubility increases with decrease of temperature

until the two liquids mix in all proportions. In the same way, triethylamine and water mix in all proportions at low temperatures, but gradually separate as the temperature rises (*loc. cit.*). In both these cases, the substances are insoluble in water, but form at low temperatures hydrates which are soluble in water and in the compounds themselves. With bromine, a very soluble hydrate is formed at low temperatures, which is gradually dissociated as the temperature rises and the solubility decreases. Water is quite insoluble in bromine.

The author next studies the thermochemical relations of the above liquids. When a simple solution takes place, the heat evolved is always negative, and is greatest when the two liquids are mixed in equal parts. When combination occurs, the heat evolution is the algebraical sum of the + heat due to combination, and − heat due to solution of the compound formed in excess of one of the constituents. Hence with isobutyl alcohol and water, for instance, the heat of solution changes sign at that temperature at which the curve of solubility shows a minimum.

Finally the author studies the effect of the state of aggregation on solution. He finds that if mixtures of salicylic or benzoic acid and water are heated to the temperature at which they mix in all proportions and are then cooled to a given temperature, solutions are obtained which contain less substance than if the constituents had been simply left in contact at the given temperature. Moreover, on further cooling of a solution obtained by the first method, the substance separates out in the liquid state, whilst the solid is obtained on cooling a solution prepared by the second method. The author considers that the compounds exist in solution in isomeric modifications in the two cases. H. K. T.

Lecture Experiments. By M. Rosenfeld (*Ber.*, **19**, 1899—1903). —1. An apparatus for electrolysing pure hydrochloric acid is described with sketch (comp. Abstr., 1885, 715). 2. This is an arrangement for showing the sublimation of sulphur in a current of carbonic anhydride. N. H. M.

Decomposition of Ammonia by Electrolysis. By A. Irving (*Chem. News*, **54**, 16).—An ordinary three-tubed voltameter is fitted with carbon electrodes, the electrolyte is a concentrated solution of sodium chloride to which is added one-tenth of its volume of strong ammonia. On passing a current from a battery of 4 to 6 Bunsen or Grove elements, gases collect in the separate tubes in the proportion of 3 vols. hydrogen in the one to 1 vol. nitrogen in the other.

D. A. L.

Ferrates: a Lecture Experiment. By C. L. Bloxam (*Chem. News*, **54**, 43).—A fragment of potassium hydroxide is placed in some ferric chloride, a few drops of bromine added, and if necessary gently heated; the mass dissolves in water, yielding a fine red solution of potassium ferrate resembling permanganate in its tinctorial power. A fine red solution of calcium ferrate is obtained by adding ferric chloride to bleaching powder and boiling with water. Manganous

sulphate destroys the colour, and filtration through paper discharges it; barium chloride produces a purple precipitate of barium ferrate.

D. A. L.

Chromammonium Compounds: a Lecture Experiment. By K. KRAUT (*Chem. Zeit.*, **10**, 820).—An apparatus is described for showing the formation of rhodo- and luteo-chromium chlorides.

Inorganic Chemistry.

Physical Properties of Bromine. By J. D. VAN DER PLATTS (*Rec. Trav. Chim.*, **5**, 34—80).—After a list of the points of solidification, fusion, and ebullition, given for bromine by various writers, and allusion to the difficulties experienced in removing water and other halogens, the author describes his method of purification of this element, which is based on that adopted by Stas. This method consists in the distillation of commercial bromine, purified by washing with water, in presence of purified potassium bromide and zinc oxide; the bromine is then washed with water at 65°. The product thus obtained is free from chlorine and iodine, but probably contains bromoform; it is finally dried by calcium bromide prepared from the bromine previously obtained and rectified over phosphoric anhydride. The boiling point of the specimen thus obtained was 63·03° at 759·5 mm., as a mean of five concordant experiments, the point of fusion — 7·3 (mean of four concordant experiments), but the point of solidification varied from — 8·5 to — 14 (comp. Ramsay and Young, Trans., 1886, 453); its sp. gr. at 0° compared with water at 4° = 3·1875, which agrees with the determinations of Thorpe and Balard. As a guarantee of the purity of the specimen of bromine, it was converted into hydrobromic acid by phosphorus and water, and the relation of bromine to silver determined; the ratio found was practically identical with that obtained by Stas. The acid obtained was also shown to be free from hydriodic and hydrochloric acids.

V. H. V.

Electrolysis of Hydrogen Fluoride. By H. MOISSAN (*Compt. rend.*, **102**, 1543—1544).—When anhydrous hydrogen fluoride is electrolysed in a platinum tube by means of a battery of 50 Bunsen elements, hydrogen is liberated at the negative pole, whilst at the positive pole a gas is evolved which is completely absorbed by mercury with formation of mercurous fluoride, and which decomposes water with production of ozone. Phosphorus when introduced into the gas ignites spontaneously and forms phosphorus fluorides, sulphur melts, carbon seems to remain unaltered, dry potassium chloride is decomposed with liberation of chlorine, and crystallised silicon ignites spontaneously and burns brilliantly with formation of silicon fluoride. The positive electrode of iridio-platinum was corroded whilst the negative electrode was unaltered. The gas is probably fluorine but might possibly be hydrogen perfluoride or even a mixture of hydrogen fluoride and ozone.

C. H. B.

Non-metallic Fluorides. By Guntz (*Compt. rend.*, **103**, 58).—Various non-metallic fluorides can be obtained by heating lead fluoride with non-metallic chlorides, such as carbon tetrachloride, sulphur chloride, phosphorus trichloride and oxychloride. The action of phosphorus oxychloride on lead fluoride affords a very convenient method of preparing phosphorus oxyfluoride. C. H. B.

Method for Preparing so-called Pentathionic Acid. By T. Salzer (*Ber.*, **19**, 1696—1697).—When 10 c.c. of decinormal sodium thiosulphate solution is treated with a drop of a solution of potassium aresenite containing 1 per cent. of arsenic trioxide, and with an excess of hydrochloric acid, the solution becomes turbid and has a slight odour of hydrogen sulphide; after a long time arsenic sulphide and a little sulphur are precipitated. When filtered the solution gives the reactions of pentathionic acid. N. H. M.

Conditions necessary for the complete Removal of Arsenic from Hydrochloric Acid by Hydrogen Sulphide. By R. Otto (*Ber.*, **19**, 1903—1910).—Pure hydrochloric acid was found, even after prolonged treatment with hydrogen sulphide, to contain traces of arsenic, and is therefore not suited for the detection of metallic poisons. The author has found that crude hydrochloric acid can be readily freed from arsenic by treatment with hydrogen sulphide. It is diluted until the sp. gr. is 1·12, saturated with hydrogen sulphide, and allowed to remain in a closed vessel for 24 hours at 33—40°; it is then decanted, filtered, and distilled until $\frac{1}{10}$th remains in the retort. Pure hydrochloric acid can be purified by means of hydrogen sulphide if it is first treated with a small quantity of ferric chloride, potassium dichromate, arsenious acid, &c. N. H. M.

Berthollet's Explosive Silver. By F. Raschig (*Ann.*, **233**, 93—101).—The results of a series of analyses of explosive silver show that this substance consists of a mixture of Ag_3N with varying quantities of metallic silver. Dilute sulphuric acid dissolves the explosive compound but leaves the metallic silver undissolved. Explosive silver is best prepared by dissolving freshly precipitated silver oxide in strong ammonia. The compound is deposited from this solution either by exposure to the air, by the application of gentle heat, or by the addition of alcohol. W. C. W.

Hydrated Barium Hydroxide. By De Forcrand (*Compt. rend.*, **103**, 59—61).—The compound, $BaO,2MeOH + 2H_2O$ (this vol., p. 861), when heated at 135° in a current of dry hydrogen, does not give the compound $3BaO,4MeOH$, but is converted into the hydroxide, which retains a small quantity of methyl alcohol. If it is allowed to remain in a vacuum at the ordinary temperature a hydrate, $BaH_2O_2 + H_2O$, is obtained. The heat of formation of this hydrate is very small:—

BaH_2O_2 solid + H_2O liquid = $BaH_2O_2{\cdot}H_2O$ solid develops + 1·52 cal.
BaH_2O_2 ,, + H_2O solid = $BaH_2O_2{\cdot}H_2O$,, ,, + 0·08 ,,

When this hydrate is dissolved in methyl alcohol the thermal disturbance gives for the heat of formation of the compound, $BaO,2MeOH + 2H_2O$, the value + 40·18 cal., which agrees closely with that previously found (40·78).

The mutual conversion of these compounds is in agreement with their heats of formation and tensions of dissociation. The formation of the alcoholate, 3BaO,4MeOH, instead of the hydroxide, when an alcholic solution of the compound $BaO,2MeOH + 2H_2O$ is heated, depends on the fact that as soon as the compound separates in the solid form in presence of an excess of methyl alcohol, the tension of the methyl alcohol in the compound becomes negligeable, whilst that of the water present continues to be important.

C. H. B.

Setting of Cement. By E. Michel (*J. pr. Chem.* [2], **33**, 548—558).—According to the experiments herein detailed, the setting of cement is dependent, firstly on the addition of water, which should be as limited and uniform as possible; secondly, on the density and intimate mixture of the materials, and thirdly, on the formation of calcium carbonate. Of the three principal constituents of cement, silica, lime and alumina, all are chemically active, but the proportion of lime need only be slight; the alumina determines the rapid setting but the silica the permanent hardening. The chemical change which conditions the setting only takes place to a slight degree, and is principally restricted to the surface. Analyses are given to prove that on an average not more than 5 per cent. of the material becomes chemically combined. The alkalis play no important part in the setting. V. H. V.

Setting of Cement. By L. C. Levoir (*Rec. Trav. Chim.*, **5**, 59—64).—According to the author's experiments, the hardening of Portland cement depends on the disruption of each granule of the cement after it has been baked and moulded; it is then covered with moisture and calcium carbonate; colloid silicates are also formed, which are gradually converted into crystalline modifications, a change dependent on the temperature. Experiments are quoted to show that the silica plays the most important part in the process. Cements, otherwise good, were shown to give efflorescent deposits on their surfaces, some of calcium sulphate due to the sulphur of the coke used in the manufacture, others of sodium carbonate, from the conversion of sodium silicate into carbonate by access of air. V. H. V.

Thallium in Crude Zinc. By Kosmann (*Chem. Zeit.*, **10**, 762—763).—A sample of crude zinc obtained by melting up zinc waste contained 1·4 per cent. of thallium. This is the first time thallium has been found as a constituent of crude zinc. D. A. L.

New Cuprammonium Iodide. By A. Saglier (*Compt. rend.*, **102**, 1552—1555).—100 grams of an ammoniacal solution of cupric oxide containing 7 to 8 per cent. is mixed with an equal weight of a 10 per cent. solution of iodine in alcohol. A brown precipitate of

nitrogen iodide is formed, but this readily disappears on warming, and if the liquid is heated for about an hour on the water-bath it becomes green, and deposits brilliant green needles which must be dried as quickly as possible. They have the composition $4NH_3,Cu_3I_4$ or $4NH_3,Cu_2I_2,CuI_2$, and are intermediate between cuprosammonium iodide and cuprammonium iodide. They are more stable than cuprosoammonium iodide, but alter rapidly when exposed to air, losing ammonia and iodine, and eventually changing to cuprous iodide. When carefully heated, iodine and ammonia are given off and a residue of cuprous oxide is left. The crystals are insoluble in water but are decomposed by very prolonged ebullition. They are only decomposed by potash after prolonged boiling, but they dissolve readily in ammonia, and the solution yields cuprammonium iodide when evaporated.

If the green solution obtained as above is boiled with metallic copper until it becomes colourless and is then allowed to cool, it deposits cuprosoammonium iodide in brilliant white needles 5—6 mm. long.

If the mixture of ammoniacal copper solution and alcoholic iodine is allowed to stand with exposure to air at the ordinary temperature, the nitrogen iodide slowly dissolves, and after some hours the liquid deposits cuprammonium iodide in octahedral crystals. If the ammoniacal solution is boiled with iodine for several hours without addition of alcohol and is then cooled, it deposits cuprammonium iodide in tetrahedral crystals.

Cuprammonium tetriodide, $4NH_3,CuI_2,I_2$, is obtained in brilliant black crystals, green by transmitted light, by boiling 100 c.c. of the ammoniacal copper solution with 20 grams of iodine, and allowing the liquid to cool. If a further quantity of 20 grams of iodine is dissolved in the mother-liquor from these crystals, the liquid on cooling deposits *cuprammonium hexiodide*, $4NH_3,CuI_2,I_4$, in rectangular tablets, which are brown by transmitted light. This compound is usually obtained by mixing a warm solution of cuprammonium nitrate with a solution of iodine in potassium iodide. C. H. B.

Mercurous Sulphate. By G. Buchner (*Chem. Zeit.*, **10**, 759—760 and 790—791).—Mercurous sulphate was exposed under various conditions to air, light, moisture, and darkness: numerical data are given from observations extending over three years, and it is shown that light acts to a certain extent on this salt, but nevertheless when exposed under the most adverse conditions the change produced—the decomposition extending only in one case to 14 per cent. of the mercurous sulphate—was never so great as to justify the classification of this salt amongst the very unstable compounds. It is best preserved in a moist state in presence of metallic mercury; or if dry it should fill a well-stoppered bottle and should be kept in the dark. The change into mercury and mercuric sulphate is reversed by the action of water, therefore for electrical purposes the slight decomposition of mercuous sulphate is of no consequence. For analysis, the mixture of mercurous and mercuric sulphates is digested with dilute hydrochloric acid; the mercuric salt remains in solution whilst the

mercurous salt is precipitated as chloride. In the presence of mercury, the mercuric sulphate is also changed into mercurous chloride, therefore when such a change would be detrimental to the results required, titration with iodine and potassium iodide is resorted to. Treating the mixture with water and observing the formation of yellow $HgSO_4,2HgO$, does not answer with less than 10 per cent. of mercuric salt present. D. A. L.

Yttria. By W. Crookes (*Chem. News*, **54**, 32—40).—The author takes exception to the use of the name "yttria" in any but its usual sense, and protests against its application, at least at present, to any of the substances separated from yttrium, and provisionally designated $G\alpha$, $G\beta$, $G\gamma$, $G\delta$, $G\epsilon$, $G\zeta$, $G\eta$. Moreover, he contends that these are constituents and not impurities.

Owing to dissension with reference to the earth giving rise to the pair of greenish-blue bands (mean λ 545), it is thought better to speak of it as $G\beta$ 545. The identity or non-identity of $G\delta$ with $Z\alpha$, or $G\beta$ with $Z\beta$ is not yet proved, any way the author does not wish to claim $Z\alpha$ and $Z\beta$ amongst his new elements. D. A. L.

Thorium, Potassium, and Zirconium Potassium Phosphates. By L. Troost and L. Ouvrard (*Compt. rend.*, **102**, 1422—1427).—If the oxide, amorphous phosphate, or anhydrous chloride of thorium is added to fused potassium metaphosphate so long as it will dissolve, the mixture allowed to cool slowly, and then extracted with acidified water, an insoluble residue is left, which consists of minute rhombic prisms acting strongly on polarised light; sp. gr. at 12° = 5·75. They are insoluble in hydrochloric or nitric acid and in aqua regia, and have the composition $K_2O,8ThO,3P_2O_5$ (Th = 116·2), or $K_2O·4ThO_2,3P_2O_5$ (Th = 232·4).

The corresponding zirconium compounds, when treated in the same way, dissolve more readily, and the insoluble product consists of hexagonal crystals, which act strongly on polarised light; sp. gr. at 12° = 3·18. They are insoluble in aqua regia, and have the composition $K_2O,4ZrO_2,3P_2O_5$.

With potassium pyrophosphate, thorium compounds yield microscopic octahedra, which act on polarised light; sp. gr. at 7° = 4·688. They dissolve in nitric acid, and have the composition $K_2O,2ThO,P_2O_5$, or K_2O,ThO_2,P_2O_5. Larger crystals are obtained if the potassium pyrophosphate is mixed with some potassium chloride.

Zirconium compounds under the same conditions yield colourless hexagonal lamellæ, which give a black cross surrounded by coloured rings when examined by polarised light; sp. gr. at 7° = 3·076. They are insoluble in aqua regia, but dissolve in hot concentrated sulphuric acid, and have the composition $K_2O.ZrO_2,P_2O_5$.

With tripotassium phosphate, the thorium compounds yield hexagonal lamellæ, which behave with polarised light like crystals with a negative axis, or with two axes which almost coincide; sp. gr. at 12° = 3·95. They dissolve in acids, and have the composition

$$3K_2O,3ThO_2,2P_2O_5, \text{ or } 6K_2O,3ThO_2,4P_2O_5.$$

If the mixture of the thorium compound and potassium phosphate is heated until the alkaline salt volatilises, thorium oxide is obtained, crystallised in cubo-octahedra and rhombic dodecahedra of the regular system; sp. gr. at 15° = 9·876.

The zirconium compounds also dissolve in fused tripotassium phosphate, but when the cooled product is treated with water, the residue consists of altered crystals and an amorphous substance. If the phosphate is mixed with some chloride, the residue consists of hexagonal lamellæ, identical with those obtained when potassium pyrophosphate is used.

If the fused mixture is heated to a very high temperature, zirconium oxide is obtained, crystallised in quadratic prisms terminated by pyramids; sp. gr. at 17° = 5·726.

The compounds formed by zirconium and thorium with fused potassium metaphosphate or pyrophosphate are analogous in composition, but are not isomorphous. With potassium orthophosphate, the products are not analogous in composition. Crystals of thoria and zirconia obtained at a high temperature are not isomorphous.

C. H. B.

Chemistry of Manganese and Fluorine. By O. T. Christensen (*J. pr. Chem.* [2], **34**, 41—46).—By treating a solution of manganese dioxide in hydrochloric acid with excess of sodium pyrophosphate, a double salt, $Mn_2Na_2P_2O_7 + 10H_2O$, is obtained, the composition of which confirms Pickering's view as to the constitution of manganic chloride (Trans., 1879, 654). The corresponding fluoride is also Mn_2F_6, and not MnF_4, and yields double salts, $4KF,Mn_2F_6$, &c., strictly comparable with the double salts of aluminium, iron, and chromium; a manganese compound, analogous in composition to cryolite, was also obtained.

The author has also made some determinations of the atomic weight of fluorine, starting with ammonium manganifluoride, treating this with hydrochloric acid and potassium iodide, and estimating the amount of iodine set free. He finds F = 19 when O = 16.

By the electrolysis of a solution of Mn_2F_6 in hydrofluoric acid, permanganic acid is formed; this reaction is very delicate. Heated in a current of oxygen, the manganifluorides give off a gas, which sets free iodine from potassium iodide.

J. K. C.

Nickel Carbide. By L. Pebal (*Annalen*, **233**, 160—165).—Nickel obtained by the reduction of the oxide by charcoal at a white heat, may contain as much as 1·4 per cent. of carbon. On treatment with acids the metal dissolves, leaving a residue of graphite. One specimen of the nickel containing 0·98 per cent. of graphite, and 0·28 per cent. of combined carbon, was melted in a graphite crucible, and rapidly cooled in an iron mould, and the product analysed. It now contained 0·78 per cent. of graphite and 0·61 per cent. of combined carbon.

W. C. W.

Decomposition by Heat of Potassium Chloro- and Fluo-chromate. By A. C. Oudemans (*Rec. Trav. Chim.*, **5**, 111—117).—The decomposition by heat of potassium chlorochromate has been explained

in various ways; according to Schafarik chromyl chloride and potassium chromate are formed, but according to Streng chlorine is produced, thus: $6CrO_2(Cl\cdot OK = K_2Cr_2O_7 + 2K_2CrO_4 + Cr_2O_3 + 3Cl_2$. The author has more fully examined this question by determinations of the chlorine evolved, the loss in weight, and thus by difference the oxygen evolved. The results are in accordance with the equation $4CrO_2Cl\cdot OK = K_2Cr_2O_7 + Cr_2O_3 + 2KCl + Cl_2 + O_3$.

Experiments with potassium fluochromate gave similar results.

V. H. V.

Uranium Compounds. By G. Alibegoff (*Annalen*, **233**, 117—143).—*Uranium tribromide* is prepared by heating the tetrabromide in a current of dry hydrogen. It closely resembles the trichloride in its appearance and properties. The tetroxide has been previously described by Fairley (this Journal, 1877, i, 127), and by Zimmermann (this vol., p. 598).

The author was unable to prepare in the wet way the two silver salts, $Ag_2U_2O_7$ and $Ag_2U_2O_{11}$, described by Guyard (*Bull. Soc. Chim.*, **1**, 95), but a salt having the composition of the former is obtained by fusing a mixture of silver nitrate and dry potassium uranate. It is an amorphous powder, of a yellowish-red colour, insoluble in water, but freely soluble in dilute acids.

Uranium sesquisulphide, U_2S_3, is formed by passing sulphuretted hydrogen over warm uranium tribromide in an apparatus from which every trace of atmospheric air is carefully excluded. The sulphide is a black powder, insoluble in hydrochloric and in dilute nitric acid. It evolves sulphuretted hydrogen on exposure to the air, and burns when heated on platinum foil. It is reduced to the monosulphide US by reduction in hydrogen at a red heat.

W. C. W.

Action of Vanadic Anhydride on Haloïd Salts of the Alkalis. By A. Ditte (*Compt. rend.*, **103**, 55—58).—When warm solutions of potassium iodide and soluble vanadic anhydride are mixed together, iodine is liberated, and green lustrous crystals of the hypovanadate $K_2O,2V_2O_4 + H_2O$ are precipitated. If the mother-liquor is boiled and then concentrated, it deposits yellow crystals of the vanadate $2K_2O,V_2O_5$.

If the iodide and vanadic anhydride are fused together in a crucible out of contact with oxygen, iodine is liberated, and a brilliant black residue is left, which, when treated with warm water, yields a reddish-yellow solution, which deposits dark green crystals of the anhydrous hypovanadate $K_2O,2V_2O_4$, leaving a yellow liquid, from which the vanadate $K_2O,V_2O_5,16H_2O$ crystallises after concentration.

Potassium bromide added to a hot solution of vanadic anhydride precipitates the insoluble variety, but no reduction takes place. If the two substances are fused together out of contact with oxygen, bromine is liberated, and potassium hypovanadate and vanadate, with some unaltered vanadic anhydride are left, but decomposition takes place much less readily than with the iodide.

With potassium chloride, the phenomena are similar, but the action at a high temperature is even less than with the bromide.

When soluble vanadic anhydride is added to a boiling solution of potassium cyanide, the liquid becomes colourless, and carbonic anhydride and nitrogen are given off, and if the vanadic anhydride is added in excess a red liquid is obtained, which, when concentrated, deposits crystals of the vanadate $K_2O,V_2O_5 + 3H_2O$, whilst hypovanadic acid remains mixed with the unaltered vanadic acid. If the potassium cyanide is in excess, the whole of the vanadic anhydride is reduced, a small quantity being even converted into the trioxide. This last oxide is the sole product obtained when potassium cyanide and vanadic anhydride are fused together.

Similar results are obtained with the corresponding sodium and ammonium salts. The behaviour of fluorides is different.

C. H. B.

Atomic Weight of Antimony. By A. Popper (*Annalen*, **233**, 153—160).—In his investigation of the composition of explosive antimony, Pfeiffer (Abstr., 1882, 467) found the electrolytic equivalent of antimony to be 40·34, corresponding with the atomic weight 121. The author has carefully redetermined the electrolytic equivalent of the metal, and has arrived at the same result. He suggests that the difference between this value and that obtained by Cooke (119·6) is probably due to the presence of germanium or other rare metal.

W. C. W.

Action of Acids and Bases on Solutions of Tartar Emetic. By Guntz (*Compt. rend.*, **102**, 1472—1474).—When a dilute solution of tartar emetic is mixed with an equivalent quantity of hydrochloric acid, the whole of the antimony is not precipitated, and the precipitate is not antimony hydroxide (comp. Clarke and Stallo, Abstr., 1881, 156). With one equivalent of hydrochloric acid, 10·5 per cent. of the total antimony is precipitated, and the amount increases with the proportion of acid until 16 equivalents precipitate 58 per cent. Precipitation is diminished by diluting the solution of tartar emetic, and is increased by a rise of temperature. The precipitate contains tartaric acid, chlorine, and antimony oxide in proportions which vary with the conditions of precipitation and washing. The quantity of antimony precipitated by sulphuric acid is even less than by hydrochloric acid.

It is most probable that when tartar emetic is mixed with hydrochloric acid, potassium chloride and antimony hydrogen tartrate are formed. The latter is decomposed by water into tartaric acid and basic antimony tartrate, which is acted on by the excess of hydrochloric acid with formation of the oxychloride, $Sb_4O_5Cl_2$. This view is confirmed by the behaviour of barium antimony tartrate. If this salt is treated with an equivalent quantity of sulphuric acid, pure barium sulphate is precipitated, and pure antimony hydrogen tartrate remains in solution. If now this solution is mixed with hydrochloric acid, basic antimony tartrate containing chlorine is precipitated; if, on the other hand, dilute sulphuric acid is mixed with a corresponding quantity of solid barium antimony tartrate, the barium sulphate which is formed always contains tartaric acid and antimony oxide, in proportions which vary with the dilution and the temperature.

When a solution of tartar emetic is mixed with 2 equivalents of

potassium hydroxide, 96 per cent. of the antimony is precipitated, and any variation from this proportion of potash is accompanied by a diminution in the amount of antimony thrown down. With ¼ equivalent, only 23 per cent. of the antimony is precipitated, whilst with 16 equivalents the precipitate is completely re-dissolved. The potassium hydroxide forms normal potassium tartrate and antimony oxide, and the latter combines with the excess of alkali, forming a soluble antimonite. C. H. B.

Constitution of Double Platinum Salts. By S. M. Jörgensen (*J. pr. Chem.* [2], **33**, 409—538).—This paper contains an account of the preparation of various complex compounds of the chlorides of platinum with those of ammonium and other bases, such as pyridine, ethylamine, propylamine, or various mixtures of them, made with a view of throwing more light on the constitution and isomerism of the ammonium platinum compounds. It is shown as an important point, that platosemidiammonium chloride with pyridine and platosemidipyridine chloride with ammonia give the same salt; on the other hand, platosammonium chloride with pyridine or the corresponding pyridine salt with ammonia give identical salts, but isomeric with the above. Precisely similar results were obtained with ethylamine. The crystallographic forms, as also the dichroic nature of the various salts obtained, are described in full.

Among other compounds mentioned are copper dipyridine sulphate, $4C_5H_5N,CuSO_4$, which crystallises in deep blue prisms, and also a corresponding dithionate, a light blue precipitate, consisting of large rhombic prisms. V. H. V.

Mineralogical Chemistry.

Products of the Eruption of Mount Etna, 1886. By L. Ricciardi (*Compt. rend.*, **102**, 1484—1487).

	1.	2.	3.	4.
SiO_2	49·25	49·27	49·33	48·45
Cl	traces	—	—	traces
P_2O_5	1·22	0·92	1·07	0·88
Al_2O_3	16·16	15·13	15·45	15·42
Fe_2O_3	3·21	3·72	3·41	2·36
FeO	10·32	10·28	10·12	13·20
MnO	0·22	0·31	0·36	0·42
CrO	0·09	0·06	0·08	0·13
CaO	9·94	9·85	10·03	11·12
MgO	4·96	3·81	3·56	4·87
K_2O	1·17	1·94	1·78	0·91
Na_2O	2·64	4·53	4·49	2·93
Loss on heating	1·12	0·35	0·41	0·17
	100·30	100·17	100·09	100·86

(1.) A blackish magnetic sand, which fell at Cibali on May 23. It consists of amorphous matter mixed with crystalline fragments of labradorite, olivine, and pyroxene. It contains 1·32 per cent. of salts which dissolve in water, forming an acid solution, and it is easily decomposed by hot mineral acids, with evolution of a small quantity of hydrogen sulphide; sp. gr. at 22° = 2·474. (2.) Ash which fell at Cibali during the night of May 28—29th. (3.) Ash which fell at Cantane at the same time. This ash resembles No. 1, but contains 2·68 of soluble matter with an alkaline reaction, and also contains small quantities of sulphates. (4.) Lava from Mount Terror, the new crater which opened at about 1400 metres above the sea-level. It has a deep grey colour, contains crystals of labradorite, pyroxene, and olivine, and has the general characteristics of lava from Etna. It gives an alkaline reaction to water, and is partially decomposed by hot mineral acids; sp. gr. at 22° = 2·757. It contains traces of sulphuric acid, titanium, and lithium. The close similarity in chemical composition affords further proof of the supposition that the sand, ashes, stones, &c., ejected from the volcano are products of the attrition of the lava. C. H. B.

Mineral Waters of Saint Nectaire (Puy de Dome). By G. F. Boutet (*Ann. Chim. Phys.* [6], **7**, 536—561).—There are seven separate springs of mineral water at Saint Nectaire, of two of which the author has made an exhaustive chemical and spectroscopic analysis, and has included in his paper a fully detailed description of the methods of analysis employed.

The Mont Cornador spring has a temperature of 39°, and that known as "Source Rouge" a temperature of 23°. The water from both springs has a slightly sulphurous odour, and although perfectly limpid on issuing from the granite rock, gradually becomes turbid, and of a yellowish colour, forming an encrusting deposit.

The results of the analyses given in grams per litre are as follows:—

	Source Rouge.	Source du Mont Cornador.
Free carbonic anhydride	1·7042	1·0721
Oxygen and nitrogen	not estimated	not estimated
Sodium oxide	2·4670	1·9840
Lithium oxide	0·0667	0·1064
Potassium oxide	traces	0·0003
Rubidium oxide	traces	0·0008
Cæsium oxide	traces	0·0017
Calcium oxide	0·2787	0·2930
Magnesium oxide	0·1390	0·0376
Ferric oxide	0·0107	0·2568
Barium oxide	traces	absent
Aluminium oxide	0·0330	0·0239
Silica	0·0861	0·1030
Combined carbonic anhydride	not estimated	not estimated
Hydrogen chloride	1·4945	1·3359

	Source Rouge.	Source du Mont Cornador.
Sulphuric acid	0·1061	0·0890
Boric acid	0·0043	0·0027
Phosphoric acid	traces	absent
Iodine	traces	absent
Arsenic	0·000009	traces
Organic matter	0·0078	0·0062

A. P.

Potable Water at Royat (Puy de Dome). By J. F. Boutet (*Ann. Chim. Phys.* [6], **7**, 562—570).—The water is clear, colourless, tasteless, and has no odour. The following are the results of the chemical analysis, given in grams per litre :—

Hydrogen calcium carbonate	0·02230
Hydrogen magnesium carbonate	0·00530
Sodium sulphate	0·00547
Calcium chloride	0·00891
Magnesium chloride	0·00051
Sodium chloride	0·00371
Potassium and sodium silicate	0·04280
Total solids	0·08300

A. P.

Organic Chemistry.

Polymerisation of Cyanogen Bromide. By E. Mulder (*Rec. Trav. Chim.*, **5**, 84—98).—Cyanogen bromide cannot be polymerised when heated with ether according to the statement of Eghis (*Ber.*, **2**, 159), but when heated by itself in sealed tubes, and even kept for some time at the ordinary temperature, it is gradually converted into a yellow amorphous mass, of composition corresponding with the formula nCNBr. It appears that a small quantity of bromine present assists the process of polymerisation, probably from the formation of some intermediate compound. At ordinary temperatures, the polymeric modification is decomposed by water into cyanuric acid, carbonic anhydride, and free bromine. The author considers that the polymeride at first formed has the composition $C_3N_3Br_3{\cdot}NCBr$, but as the stability towards water is increased with the length of time during which the substance is preserved, it seems to be gradually decomposed into a less complex modification of composition $C_3N_3Br_3$.

V. H. V.

Reaction of Cyanogen Bromide with Ethyl Alcohol. By E. Mulder (*Rec. Trav. Chim.*, **5**, 65—83).—According to the author, the formation of ammonium bromide and carbonic anhydride as pro-

ducts of the reaction of cyanogen bromide with ethyl alcohol, can be best explained by means of the equations (1) $CNBr + EtOH = HBr + EtCNO$, (2) $HBr + EtOH = EtBr + H_2O$, and (3) $EtCNO + OH_2 = NH_2{\cdot}COOEt$, while the carbonic anhydride is formed thus: $CNBr + 2H_2O = NH_2,Br + CO_2$. As a subsidiary product, there is obtained a crystalline compound, $C_{18}H_{15}N_2Br_2O_4$, which melts at 121°, and yields a compound $C_7H_{14}N_2O_4$, insoluble in water, sparingly soluble in alcohol; this decomposes at 270° without fusion. The latter formulæ are provisional. Ethyl carbonate was not obtained under the conditions of the experiment. V. H. V.

Derivatives of Cyanuric Acid. By E. Mulder (*Rec. Trav. Chim.*, **5**, 99—110).—If crude ethyl cyanate is allowed to stand, the proportion of ethyl cyanurate increases gradually. To determine the latter, bromine-water was found to be preferable to mercuric chloride. Saponification by aqueous solution of soda gives satisfactory results, only provided that the chemical change is complete. Ethyl cyanurate absorbs one or two molecules of hydrochloric acid to form additive products; diethylcyanuric acid absorbs one molecule of the same gas. Ethyl cyanurate is very soluble in ethyl iodide, but a dilute aqueous solution of ammonia converts it into ethyl monamidocyanurate. V. H. V.

Normal Dinitriles. By L. Henry (*Compt. rend.*, **102**, 1481—1484).—The author has previously shown that an increase of the number of cyanogen-groups in a molecule lowers the boiling point of the latter, but this influence is only exerted when the cyanogen-groups are in union with the same carbon-atom, and disappears if they are separated by CH_2.

The boiling point of malono-dinitrile (this vol., p. 786) is 218—219°, or 244° higher than that of cyanogen, a difference even greater than that between the boiling points of ethyl cyanoacetate and ethyl cyanoformate. In this case, however, the effect of the contiguity of the two cyanogen-groups is not completely neutralised by the introduction of one CH_2 group; it only disappears when they are separated by $CH_2{\cdot}CH_2$. The difference between the boiling points of malono-dinitrile, $CNCH_2CN$, and succino-dinitrile, $CN(CH_2)_2CN$, is 46°, whilst that between succino-dinitrile and pyrotartaro-dinitrile, $CN(CH_2)_3CN$, is only 10°.

An analogous phenomenon is observed with respect to the freezing points of these compounds. Cyanogen, malono-dinitrile, and succino-dinitrile solidify readily to ice-like masses, but pyrotartaro-dinitrile does not solidify even at −23°. C. H. B.

Water of Crystallisation of Sodium Ferrocyanide. By L. Pebal (*Annalen*, **233**, 165).—Sodium ferrocyanide, $Na_4Fe(CN)_6$, forms transparent yellow crystals, which slowly become opaque on exposure to the air. The salt contains 10, not 12, mols. H_2O. W. C. W.

Ammonium Calcium Ferrocyanide. By T. Salzer (*Ber.*, **19**, 1697).—When potassium ferrocyanide is added to a concentrated solution of ammonium chloride containing calcium chloride, a crystalline precipitate of ammonium calcium ferrocyanide, $Am_2CaFeCy_6$, is

formed. Magnesium salts behave in a manner similar to calcium salts in this respect. N. H. M.

Action of Barium Monoxide on Methyl Alcohol. By De Forcrand (*Compt. rend.*, **102**, 1557—1559).—The compound

$$3BaO,4MeOH,$$

previously described (this vol., p. 781), is readily formed with methyl alcohol containing as much as 2—3 per cent. of water, the water being expelled with the excess of alcohol when the product is dried in hydrogen at 135°. If, however, the liquid is allowed to evaporate over potash and sulphuric acid at the ordinary temperature, brilliant prisms are obtained, which may be dried in an atmosphere saturated with the vapour of methyl alcohol. These crystals have the composition $BaO,2MeOH + 2H_2O$, and are soluble in water and in alcohol. If the alcoholic solution is evaporated at the ordinary temperature, it yields the same crystals, but if evaporated in a current of hydrogen at 135°, it yields the compound $3BaO,4MeOH$.

Measurements of the heats of solution of these two compounds lead to the following conclusions:—

$2MeOH$, liquid, + BaO, solid, + $2H_2O$, liquid = $BaO,2MeOH,2H_2O$ develops + 29·74 cal.

$(n+2)MeOH$, liquid, + BaO, solid, + $2H_2O$, liquid, = $BaO,2MeOH,2H_2O$, dissolved in nMeOH, develops + 40·78 cal.

The calculated heat of formation of barium methoxide is about 25·3 cal., hence it is most probable that when barium monoxide is dissolved in methyl alcohol containing a small quantity of water the compound formed is $BaO,2MeOH + 2H_2O$. C. H. B.

Action of Water and Ammonia on Methylene Chloride. By G. André (*Compt. rend.*, **102**, 1474—1477).—When methylene chloride is heated with water in sealed tubes at 200°, it is completely decomposed with formation of hydrochloric acid, formic acid, and methyl chloride, the latter being eventually converted into hydrochloric acid and methyl alcohol. Small quantities of brown products and of carbonic oxide are also formed.

When heated with aqueous ammonia under similar conditions, methylene chloride is completely decomposed even at 140°, the products being ammonium chloride, methylamine hydrochloride, and formic acid. The latter is partially decomposed, but less readily in presence of ammonia than in presence of pure water. C. H. B.

Formation of Triethylsulphine Bromide from Ethyl Sulphide and Ethyl Bromide at the Ordinary Temperature. By R. Otto and A. Rössing (*Ber.*, **19**, 1839—1840).—Crystals of triethylsulphine bromide slowly separated from a specimen of ethyl sulphide which had been prepared by the action of ethyl bromide on potassium sulphide, and doubtless contained unaltered ethyl bromide. A. J. G.

Action of Nitromethane on some Chlorhydrins. By A. Pfungst (*J. pr. Chem.* [2], **34**, 27—41).—Nitromethane (2 mols.) was heated in a sealed tube with α-dichlorhydrin (1 mol.) at 220° for 20 hours. On opening the tube a large quantity of carbonic anhydride escaped, and the residue on fractional distillation yielded an oil boiling in a vacuum at 145—150°; this proved to be formyl-α-dichlorhydrin. Attempts to substitute formyl in place of the chlorine-atoms by heating with sodium or lead formate failed. Heated with silver acetate, aceto-α-dichlorhydrin is formed, and the same compound was also obtained by the action of nitroethane on α-dichlorhydrin. The formyl-group can also be replaced by other acid radicles if the formyl ether is heated with acid chlorides; and in this way the benzoyl ether was obtained. The action of nitromethane on α-monochlorhydrin takes place more slowly, but on similar lines, glycerol α-chlorodiformate being the final product.

When ethylene chlorhydrin is heated with nitromethane, it yields an oil of the empirical formula $C_5H_9O_3Cl$, boiling at 220°, probably a polyethylene compound, in which the formyl-group can be traced by means of alcoholic potash.

The action of the nitro-compounds on the above chlorhydrins was accompanied in every case with formation of ammonium chloride. In no instance could the presence of hydroxylamine be detected.

J. K. C.

Oxidation of Levulose. By A. Herzfeld and E. Börnstein (*Chem. Centr.*, 1886, 187).—The authors have investigated the oxidation of levulose by less drastic agents than those employed by previous observers. The substance is oxidised in boiling aqueous solution by mercuric oxide in presence of barium hydroxide. The products are glycollic acid and normal trihydroxybutyric acid. This result, together with those of Kiliani (this vol., p. 219) on the synthetic action of hydrogen cyanide on levulose, with the further evidence afforded by Popoff's law of resolution by oxidation, establish the constitutional formula $OH{\cdot}CH_2{\cdot}CO{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH$.

The authors are investigating the trihydroxybutyric acid in order to establish its identity, and are extending the method of oxidation herein described to other compounds.

The oxidising action of bromine and silver oxide in presence of water has been also investigated by the authors; the results obtained show that it is only the same order of limited oxidation.

C. F. C.

Levulose. By A. Herzfeld and H. Winter (*Chem. Centr.*, 1886, 271—273).—Solutions of levulose were oxidised by the gradual addition of bromine over a period of some weeks. After isolating the bromine by treatment with lead and silver oxides, the products of the oxidation were separated. Glycollic and trihydroxybutyric acids were identified, the latter in small quantity only.

In discussing these results, the authors call attention to the presence of trihydroxybutyric acid in molasses, and its influence on the physical properties of the latter. It is produced by atmospheric oxidation in presence of the bases employed in treating the syrup. It is

also to be remembered that this trihydroxybutyric acid is formed as a product of the digestion of sugar in the animal body.

In conclusion, the authors discuss the value of the evidence afforded by these products of oxidation as to the constitution of the various sugars oxidised: they are not yet prepared to draw final conclusions.

C. F. C.

A New Compound of Saccharose. By A. Herzfeld (*Chem. Centr.*, 1886, 271).—When the saccharates of the alkaline earths are suspended in alcohol and treated with hydrogen chloride, the compound dissolves; after some time the formation of a precipitate begins, which the author finds to be the calcium chloride double compound of an ethyl ether of the sugar. Other sugars give similar compounds. The author is pursuing the investigation of these compounds.

C. F. C.

Compounds of Hexamethylenamine with Alkyl Iodides. By A. Wohl (*Ber.*, **19**, 1840—1845).—When a large quantity of hexamethylenamine is required, it is best prepared by a method founded on Baeyer's observations, that methylal is very readily decomposed by sulphuric acid into hydrogen methyl sulphate, and an unstable compound of formaldehyde with sulphuric acid which is resolved into its components on heating. Two vols. of concentrated sulphuric acid is slowly added to 1 vol. of commercial methylal, the mixture being well cooled; 2 vols. of water is added, and the whole agitated until homogeneous. The mixture is now distilled with steam, and the evolved vapours passed into strong aqueous ammonia. The yield is about 38 per cent. of the theoretical. Hexamethylenamine is readily soluble in water and chloroform, less soluble in carbon bisulphide; it dissolves in 7 parts of hot and 14 parts of cold alcohol. Its nitrate, tartrate, and picrate were prepared.

Hexamethylenamine methiodide, $C_6H_{12}N_4,MeI$, separates from a solution of its components in absolute alcohol, after some hours, at the ordinary temperature, or is formed more quickly if the mixture is heated under pressure at 100°. It crystallises in long, white, silky needles, turns yellow at 188°, and melts at 190° with decomposition; is readily soluble in water, sparingly in hot alcohol, and is insoluble in ether, chloroform, and carbon bisulphide. When treated with silver chloride, it is converted into the corresponding chloride from which the *platinochloride*, $(C_6H_{12}N_4),Me_2PtCl_6$, was prepared as a yellow powder, melting about 205°, and nearly insoluble in water, alcohol, and ether.

When the iodide is treated with silver oxide, or with potash or soda, the hydroxide seems to be formed, but so far its instability has baffled all attempts to isolate it.

Hexamethylenamine ethiodide, $C_6H_{12}N_4,EtI$, prepared in a manner similar to the methiodide, forms white needles, turns yellow at 130°, melts at 133°, and decomposes at a slightly higher temperature.

Dihexamethylenamine methyleniodide, $(C_6H_{12}N_4)_2,CH_2I_2$, crystallises in white needles, melts at 165°, and is readily soluble in water, more sparingly in alcohol, and insoluble in ether, chloroform, and carbon

bisulphide. The iodine is completely removed from all three iodides by treatment with silver nitrate. A. J. G.

Condensation of Formaldehyde. By O. Loew (*J. pr. Chem.*, [2], **34**, 51—55).—By heating a ½ per cent. solution of formaldehyde for 12—15 hours with granulated zinc, or better with tin, a sugar is formed which agrees in most points with the formose already described. Its barium and lead compounds were prepared and analysed. It combines very quickly with phenylhydrazine, and the resulting compound shows some points of difference from that obtained with formose, notably in its colour reactions with resorcinol and diphenylamine; the sugar also reduces more Fehling's solution than formose, and the author, therefore, distinguishes it by the name of pseudoformose.

A sugar, apparently identical with formose, was obtained by boiling a dilute solution of formaldehyde with potassium carbonate, but all attempts to produce a sugar by treatment with mineral acids failed. J. K. C.

Iodaldehyde. By W. P. Bloxam and E. F. Herroun (*Chem. News*, **53**, 301—302).—The authors have failed to obtain this substance by Chautard's method (this vol., 330—331); in fact, iodine appears to be very sparingly soluble in either strong or weak solutions of pure aldehyde. By treating a mixture of alcohol and iodine, however, or better still of aldehyde and iodine, with a small quantity of strong nitric acid and digesting at 40°, the iodine disappears rapidly, and irritating vapours are evolved. After distilling below 80°, the residue when heated with water yields a heavy, pale yellow oil, agreeing very closely in properties with Chautard's iodaldehyde, but at ordinary temperatures it is only slowly decomposed by dilute acids, whereas Chautard's is instantly decomposed. With silver nitrate, it yields a precipitate of silver iodide, whilst it is decomposed by sodium carbonate, and in its aqueous solutions even by barium carbonate. D. A. L.

Decomposition Products of Thialdine Thiocyanate. By W. Marckwald (*Ber.*, **19**, 1826—1832).—Thialdine thiocyanate forms long needles, melts at 132° with decomposition, and is readily soluble in alcohol, ether, and hot water.

When boiled in aqueous solution for half hour in a reflux apparatus, it is decomposed into thioaldehyde, γ-trithioaldehyde, and a substance of the formula $C_6H_9NS_3$; the two last are precipitated together as an oil, and can be separated by distillation with steam with which the substance last mentioned does not volatilise.

Thioaldehyde, C_2H_4S, is liquid, boils at about 40°, has a very powerful odour, and is miscible with water, alcohol, and ether. Vapour-density, found = 2·22, calculated = 2·08. An oil soon separates from its aqueous solution showing the characters of a polymerised thioaldehyde; the pure aldehyde can be kept unaltered for some hours. With concentrated sulphuric acid, it is at once polymerised to β-trithioaldehyde, whilst with concentrated hydrochloric acid it yields the γ-compound. It does not yield a compound with sodium hydrogen sulphite.

Ammonia immediately converts it into thialdine, whilst with the amines it seemingly yields homologous thialdines.

γ-Trithioaldehyde, $C_6H_{12}S_3$, crystallises in white needles, melts at 76°, and boils at 242° without decomposition; it is insoluble in water, readily soluble in ether and in hot alcohol. It has the vapour-density 6·09; calculated for $C_6H_{12}S_3 = 6·24$. It thus somewhat resembles the isomeric *α*- and *β*-trithioaldehydes previously described. It only forms a single silver nitrate derivative, $C_6H_{12}S_3,AgNO_3$, which, unlike the derivatives of the isomerides, is very unstable, decomposing with separation of silver sulphide if its solution is gently warmed. It is decomposed by boiling aqueous potash into aldehyde resin, and potassium sulphide. It dissolves without decomposition in concentrated sulphuric acid.

The compound, $C_5H_9NS_3$, crystallises in white needles, melts at 138°, begins to decompose at about 170°, is nearly insoluble in cold water and alcohol, moderately soluble in ether. It yields a compound with silver nitrate, $C_5H_9NS_3,AgNO_3$, crystallising in microscopic needles, and decomposing when its solution is heated. The platinochloride, $(C_5H_9NS_3)_2,PtCl_4$, is crystalline. The substance exhibits the properties of a feeble acid, and probably has the constitution

$$S<\begin{matrix}CHMe\cdot S\\CHMe\cdot S\end{matrix}>C:NH.$$

By the action of hydrogen sulphite on a strongly acid solution of aldehyde, a substance is obtained of the formula $CHMe<\begin{matrix}O\\S\end{matrix}>CHMe$. It crystallises in long needles, melts at 60—61°, boils at 166—168° without decomposition, and is insoluble in water, readily soluble in alcohol and ether. Vapour-density, 2·61; calculated, 2·60.

A. J. G.

Action of Heat on Ketones. By P. Barbier and L. Roux (*Compt. rend.*, **102**, 1559—1562).—The vapour of the ketone was passed through a copper tube heated to bright redness, and the products were collected and condensed.

Acetone yields a very small proportion of tarry products which contain naphthalene, and a large volume of gas of the following percentage composition:—Carbonic oxide, 39·23; methane, 37·58; hydrogen, 17·54; ethylene, 5·65.

Benzophenone yields tarry products which contain a considerable proportion of benzene, a small quantity of diphenyl melting at 70°, paradiphenylbenzene melting at 205°, a certain quantity of resinous substances, and a very large proportion of unaltered benzophenone. A considerable volume of gas is also produced; it contains 80 per cent. of carbonic oxide and 20 per cent. of hydrogen, with traces of acetylene. At an incipient white heat, benzophenone is completely decomposed into carbon which contains very little hydrogen, carbonic oxide, and hydrogen in proportions which correspond with complete decomposition of the phenone.

Acetophenone is almost completely decomposed at a bright red heat, and yields a gaseous mixture with the percentage composition:—Carbonic oxide, 48·0; methane, 28·3; hydrogen, 20·0; ethylene, 3·7,

and tarry products which contain the same substances as the tarry products from benzophenone, together with a small quantity of toluene. Acetophenone, in fact, behaves like a mixture of acetone and benzophenone.

The general action of heat on the ketones is to separate the CO nucleus and liberate the fundamental hydrocarbon-groups.

C. H. B.

β-Sulphopropionic Acid. By T. Rosenthal (*Annalen*, **233**, 15—38).—β-Sulphopropionic acid is obtained by boiling a solution of ammonium β-iodopropionate with ammonium sulphite. The mixture is afterwards boiled with baryta-water to expel the ammonia, and the excess of baryta is removed by filtration. On evaporating the filtrate, the barium salt of β-sulphopropionic acid is deposited in colourless four-sided plates containing 5 mols. H_2O. The salt is soluble in hot water, but insoluble in alcohol and ether. The free acid,

$$COOH{\cdot}C_2H_4{\cdot}SO_3H,$$

forms transparent crystals, which are very hygroscopic. It is freely soluble in water and alcohol. It melts at 68°, and begins to decompose at 150°. The following salts were prepared: $COOK{\cdot}C_2H_4{\cdot}SO_3K + H_2O$, forms small prisms freely soluble in water; $COOH{\cdot}C_2H_4{\cdot}SO_3K + H_2O$, silky needles freely soluble in water; $C_2H_4(COONa)(SO_3Na) + H_2O$, indistinct crystals, very soluble in water; $COONH_4{\cdot}C_2H_4SO_3NH_4 + 4H_2O$, hygroscopic crystalline mass; $COOH{\cdot}C_2H_4{\cdot}SO_3NH_4$, small anhydrous prisms soluble in water. The strontium salt crystallises with 5 mols. H_2O, and resembles the barium salt. The calcium salt crystallises with $2\frac{1}{2}$, and also with 1 mol. H_2O. The former salt is efflorescent. The barium, strontium, and calcium salts are more soluble in hot than in cold water. The magnesium salt is obtained in four-sided prisms containing 4 mols. H_2O, when alcohol is cautiously added to the aqueous solution of the salt. Zinc and manganese form crystalline salts containing 4 mols. H_2O. $PbC_2H_4CO_2SO_3$, granular crystals slightly soluble in hot water. $CdC_2H_4CO_2SO_3 + H_2O$, thick prisms, readily soluble.

The copper salt is deposited from very dilute aqueous solutions in green needles, which do not redissolve in water even on boiling; $COOAg{\cdot}C_2H_4{\cdot}SO_3Ag + \frac{1}{2}H_2O$ crystallises in tables and dissolves freely in water; $COOH{\cdot}C_2H_4{\cdot}SO_3Ag + \frac{1}{2}H_2O$ differs in crystalline form from the normal salt. The mercurous and mercuric salts of β-sulphopropionic acid are soluble in water.

The barium and calcium salts of α-sulphopropionic acid have been previously described by Kurbatow (*Annalen*, **173**, 6).

The potassium and ammonium salts crystallise with difficulty. The cadmium salt of the α-acid forms indistinct granular crystals containing 2 mols. H_2O. The silver salt forms anhydrous needle-shaped crystals. It is more easily affected by light than the β-salt. By the action of phosphorus pentachloride on sodium β-sulphopropionate, the chloride is obtained in an impure state as a solid body which is slowly decomposed by cold water. On treatment with alcohol, the ethylic salt of monochloro-β-sulphopropionic acid is formed. It partially decomposes on distillation.

The *diethylic salt of β-sulphopropionic acid* is prepared by acting on a mixture of silver β-sulphopropionate and dry sand with ethyl iodide diluted with absolute ether. It is a liquid miscible with alcohol and ether. It decomposes on distillation. The crude sulphonic chloride is converted into the β-thiolactic acid described by Lovén (Abstr., 1884, 1298) by reduction with tin and hydrochloric acid.

The ammonium salt of β-sulphopropionic acid is formed when a solution of ammonium hydrogen sulphite is added to a solution of ammonium acrylate. The yield is increased if the mixture is boiled for some hours. The salt of the α-acid does not appear to be formed by this reaction.

Müller observed (this Journal, 1874, 360) that acraldehyde combines with 2 mols. of sodium or potassium hydrogen sulphite. The sodium compound, $C_3H_6O_7S_2Na_2 + 4H_2O$, crystallises in prisms. On treatment with ammoniacal silver solution, it is oxidised to β-sulphopropionic acid, not the α-acid as stated by Müller. W. C. W.

Zinc Methylethylacetate. By E. Schmidt (*Arch. Pharm.* [3], **24**, 540—542).—Some time ago A. Renard obtained an acid by the dry distillation of colophony; it had the formula $C_5H_{10}O_2$, and showed great analogy to valeric acid. The author holds that it bears a stronger resemblance to methylethylacetic acid. To obtain further light on the subject, he has investigated the zinc salt of this acid. Freshly precipitated zinc oxide readily dissolves in a dilute solution of the acid; on evaporating the solution thus produced in a vacuum, very slender, white, silky crystals separate. The salt is easily soluble in cold, as well as in warm water. If a cold saturated solution be heated, white flocks separate, which however redissolve on cooling. The freshly prepared moist salt readily dissolves in water, whilst the dried salt, on the contrary, is scarcely wetted by the water, and only dissolves with difficulty. The crystallised salt is anhydrous. Dried over sulphuric acid, or for a short time at 100°, the weight remains constant. But long drying at 100° results in the separation of methylethylacetic acid with formation of a basic salt. J. T.

Oxidation of Pure Myristic Acid by Nitric Acid. By H. Noerdlinger (*Ber.*, **19**, 1893—1899).—The myristic acid employed was prepared from bicuhyba fat (this vol., p. 139), and formed lustrous scales melting at 53—54°. 100 grams of the acid were distilled with 700—800 grams of nitric acid (sp. gr. 1·3), until the liquid was homogeneous; hydrocyanic acid and carbonic anhydride were evolved. The product in the retort was found to consist chiefly of succinic and adipic acids, with a small quantity of glutaric and less pimelic, rubric, and oxalic acids. The author is also examining the volatile products of the reaction. N. H. M.

Angelic Acid. By E. Schmidt (*Arch. Pharm.* [3], **24**, 528—531).—This acid was obtained from sumbul root by Reinsch in 1844. O. Sasse, at the instance of the author, has investigated the occur-

rence of the acid in this root, and finds that the acid is a decomposition product, and does not occur as such in sumbul root. The root was extracted with light petroleum, and the solution was distilled until a pale yellow balsam-like residue was obtained. This was digested for an hour with an alcoholic potash solution, the alcohol removed, and the residue digested with water; a brownish mass crystallised out, and a considerable amount of angelic acid went into solution. To obtain the acid, the liquid was neutralised with sulphuric acid, evaporated to dryness, supersaturated with sulphuric acid and extracted with ether. Finally, after removing water, there resulted from 1 kilo. of the root about 4 grams of a liquid boiling at 180—190°, and an equal quantity boiling at 190—200°. Both distillates gave a crop of colourless crystals when placed in a cooling mixture. Those from the 180—190° liquid fused at 45°, agreed in properties with angelic acid, whilst those from the 190—200° fraction fused at 64°, and agreed with the properties of methylcrotonic acid, an isomeride of angelic acid. The two acids were produced in nearly equal amounts, and they appear to be formed simultaneously, although angelic acid is gradually converted into methylcrotonic by long boiling. J. T.

Linoleic Acid. By A. Bauer and K. Hazura (*Monatsh. Chem.*, **7**, 216—229).—The crude acid from hemp oil, prepared by saponifying the oil with soda and decomposing the sodium salt with sulphuric acid, is further purified by solution in spirit, saponification with ammonia, and precipitation of the barium salt, with subsequent saponification and extraction with ether. The pure acid gave numbers agreeing with the formula $C_{18}H_{28}O_2$, and proved to be identical with linoleic acid. When fused with potash, it yields myristic, acetic, and formic acids, together with a small quantity of azelaic acid.

When oxidised with potassium permanganate, both in the presence and absence of water, with manganese dioxide and sulphuric acid, and with hydrogen peroxide, linoleic acid yields azelaic acid. With a large excess of alkaline permanganate, it yields *sativic acid*, together with a small quantity of another substance.

Sativic acid, $C_{32}H_{62}O_{11}$, crystallises from water in brilliant microscopic needles, greasy to the touch; they melt at 160°. It is insoluble in cold water, ether, benzene, and chloroform; it is soluble in 2000 parts boiling water, in glacial acetic acid, sparingly in alcohol and in a mixture of alcohol and chloroform. The *potassium* salt, $C_{32}H_{60}O_{11}K_2 + H_2O$, crystallises in brilliant plates; the *sodium* salt crystallises in the same form, but contains 2 mols. H_2O. The *barium* salt is obtained as a white crystalline precipitate on mixing solutions of barium chloride and the sodium salt. The second substance present in the oxidation-product melts at 133°, and has the formula $C_{32}H_{62}O_9$. From the products of the action of fused potash on linoleic acid, it probably has the constitution $CH_2 : C : C_{14}H_{26}O_2$.

G. H. M.

Jervic Acid. By E. Schmidt (*Arch. Pharm.* [3], **24**, 513—522).—The author finds that jervic acid, a constituent of white hellebore, has the formula $C_5H_2O_2(COOH)_2$, and is identical with chelidonic acid.

J. T.

Chelidoninic Acid. By E. Schmidt (*Arch. Pharm.* [3], **24**, 531—534).—C. Zwenger described this acid 25 years ago. Its existence has since been much questioned. The author finds that the acid is identical with succinic acid. J. T.

Lactone of Levulose-carboxylic Acid. By H. Kiliani (*Ber.*, **19**, 1914—1915).—The *lactone* of levulose-carboxylic acid, $C_7H_{12}O_7$, is obtained by heating 5 grams of levulose hydrocyanide with 10 grams of fuming hydrochloric acid in a closed vessel. In two hours, it is treated with water, neutralised with barium carbonate, 2·5 grams of baryta dissolved in hot water is added, and the whole is evaporated until free from ammonia, treated with a further quantity of baryta, and the barium precipitated with the exact amount of sulphuric acid. The hydrochloric acid is removed by the addition of silver oxide. On evaporating the solution and allowing it to remain for some time over sulphuric acid, a crystalline mass is obtained, and this, when exposed to air for three to four weeks, yields small colourless flat prisms, which are separated from the syrup by treatment with alcohol and quickly filtering. It softens at 126° and melts at 130°. A 6 per cent. aqueous solution is strongly dextrorotary. It is soluble in ordinary alcohol. N. H. M.

Arabonic Acid and Lichenin Sugar. By R. W. Bauer (*J. pr. Chem.* [2], **34**, 46—50).—Arabinose, obtained from freshly gathered cherry gum by boiling it with dilute sulphuric acid, was allowed to remain several hours in contact with bromine and water, until it no longer reduced Fehling's solution. After removal of the bromine with lead oxide and treatment with sulphuretted hydrogen, the solution was boiled with cadmium carbonate, and the cadmium salt crystallised out by addition of alcohol; by further treatment with sulphuretted hydrogen, the arabonic acid was set free, and purified by crystallisation over sulphuric acid. It is very hygroscopic, gives by polarisation $[\alpha]_D = -67{\cdot}37°$, melts at 89°, and seems to have the formula $C_6H_{10}O_6$. The calcium salt, $(C_6H_9O_6)_2Ca + 6H_2O$, was prepared. The jelly obtained from Iceland moss was repeatedly boiled with dilute sulphuric acid until a sugar was obtained; this crystallised after standing some weeks in the cold, and when submitted to polarisation it gave $[\alpha]_D = +46{\cdot}85°$. J. K. C.

Malic Acid. By E. Schmidt (*Arch. Pharm.* [3], **24**, 535—539).—The author has found differences in the calcium salt of the acid obtained from the pure sap of (i) *bryophyllum*, dark variety; (ii) *bryophyllum*, light variety; and (iii) *sempervivum*. The amount of calcium contained in the three salts varied from 15·7 to 19·5 per cent. When dissolved in warm dilute nitric acid, the first salt alone gave a well-crystallised product. These crystals were found to agree with Hagen's analysis, as indicated by the formula $(C_4H_5O_5)_2Ca + 6H_2O$, and not with the more commonly accepted one of Braconnot, namely, $(C_4H_5O_5)_2Ca + 8H_2O$. J. T.

Calcium Malates. By F. Iwig and O. Hecht (*Annalen*, **233**, 166—172).—Hydrogen calcium malate, $Ca(C_4H_5O_5)_2 + 6H_2O$, is deposited in rhombic crystals from a solution of the normal salt in warm dilute nitric acid. It is also deposited, when calcium carbonate (1 mol.) is dissolved in an aqueous solution of malic acid (2 mols.). The author confirms Hagen's statement (*Annalen*, **38**, 263) that this salt contains 6 not 8 mols. H_2O, as given in Gmelin's Handbook. The normal salt, $CaC_4H_4O_5$, crystallises with 3 mols. H_2O, not $2\frac{1}{2}$ as stated by Hagen (*loc. cit.*). A basic salt, $Ca_2(OH)_2C_4H_4O_5$, is formed when malic acid ($\frac{1}{2}$ mol.) is mixed with 1 mol. of lime in the form of milk of lime. It appears to contain 9 mols. H_2O.

100 parts of water dissolve (I) of the acid salt, (II) of the normal salt, calculated in each case as anhydrous.

	15°.	45°.	57°.	58°.	65°.	68°.	72°.
I.	1·287	8·514	32·236	—	—	13·127	—
II.	0·839	0·711	—	0·566	0·600	—	0·663

	75°.	78°.	86°.
I.	—	7·437	—
II.	0·643	—	0·737

W. C. W.

A New Asparagine. By A. Piutti (*Ber.*, **19**, 1691—1695).—A new form of asparagine was found in the mother-liquor from crude asparagine from vetch buds. The amount obtained was 100 grams of pure product from 20 kilos. of crude asparagine, which had been extracted from 6500 kilos. of vetch buds. The results of crystallographic measurements show it to have the reverse form to ordinary asparagine; its aqueous solution has the same power of rotation as a solution of ordinary asparagine of equal strength, but is dextrorotatory. It is only slightly more soluble in water than ordinary asparagine. Both forms of asparagine yield compounds having the same chemical properties; when optically active products are formed, they have the same rotatory power but in different directions. Dextrorotatory asparagine has an intensely sweet taste. Both asparagines, when heated above 200°, yield the same product (polyfumaric acid?) When heated with 2 mols. of dilute hydrochloric acid at 170—180°, they both yield inactive aspartic acid identical with the acid obtained by Dessaignes from ammonium malate. Inactive aspartic acid is also formed when aqueous solutions of dextro- and lævo-rotatory aspartic acids are mixed and allowed to crystallise slowly. The inactive acid thus obtained differs in appearance from both active acids. N. H. M.

Thiophenaldehyde. By A. Biedermann (*Ber.*, **19**, 1853—1857; comp. Abstr., 1885, 764; this vol., p. 536).—The sp. gr. of thiophenaldehyde is 1·215 at 21° (water at 21° = 1). It shows close analogy to benzaldehyde in forming condensation products with aromatic amines and phenols. Thus when diluted with acetic acid and heated with phenol and concentrated sulphuric acid, it yields a colouring matter closely resembling benzaurin; similarly it yields green and

violet colouring matters when heated with dimethylaniline and chloropicrin. With metamidobenzoic acid, it yields a colourless compound; in this again it resembles benzaldehyde and differs from furfuraldehyde, which gives an intensely purple-red product.

Thiophenaldoxime, $C_4SH_3{\cdot}CH : NOH$, prepared in the usual manner, crystallises in long white needles, and melts at 128°.

Thienylglyoxylic acid when heated does not give a good yield of thiophenaldehyde, carbonisation occurring to some extent; about equal quantities of the aldehyde and of β-thiopenic acid being formed. Experiments to obtain a better yield have so far been unsuccessful. Its phenylhydrazide when heated at 180° is nearly quantitatively resolved into carbonic anhydride and thiophenaldehydephenylhydrazide, but the latter compound cannot be successfully resolved into the aldehyde and base.

Thiënylacrylic acid, $C_4SH_3{\cdot}CH : CH{\cdot}COOH$, is prepared by gently boiling for about seven hours a mixture of 3 parts of thiophenaldehyde, 10 parts of acetic anhydride, and 4 parts of anhydrous sodium acetate. It crystallises in strongly refractive white needles, melts at 138°, is readily soluble in the ordinary solvents, combines with bromine, and yields a pale yellow flocculent nitro-derivative when treated with fuming nitric acid. A. J. G.

Methylacetothiënone. By R. Demuth (*Ber.*, **19**, 1859—1861).—The substance previously described under this name by the author (this vol., p. 228) and prepared from coal-tar thiotolen is probably a mixture of two isomerides.

2, 5, *Methylacetothiënone*, $C_4SH_2Me{\cdot}COMe$, is obtained by treating a solution of pure β-thiotolen in light petroleum with acetic chloride and aluminium chloride. It crystallises in large colourless tables, melts at 25°, remains liquid at ordinary temperatures, and boils at 232—233° (corr.). The substance previously described could not be solidified in a freezing mixture. The phenylhydrazine compound, $C_4SH_2Me{\cdot}CMe : N_2HPh$, crystallises in tufts of pale yellow needles, and melts at 127—128°. The *acetoxime*, $C_4SH_2Me{\cdot}CMe : NOH$, crystallises in stellate groups of colourless needles and melts at 125°. *Nitromethylacetothiënone*, $NO_2{\cdot}C_4SHMe{\cdot}COMe$, crystallises in white needles, and melts at 120—121°. A. J. G.

A Second Thioxylene. By R. Demuth (*Ber.*, **19**, 1857—1859).—The known thioxylene has the constitution [$Me_2 = 2 : 5$]; to obtain an isomeric compound, γ-thiotolene was iodised, and treated in ethereal solution with methyl iodide and sodium, the mixture being well cooled; the reaction is completed after several days but the yield is very small. The new *thioxylene*, $C_4SH_2Me_2$ [$Me_2 = 3 : ?$], is liquid, has sp. gr. = 0·9777 at 21° (water at 21° = 1), and boils at 138—140°. When oxidised, this substance does not, as was hoped, yield a new thiophendicarboxylic acid, but suffers complete oxidation, only a very small quantity of resinous indefinite bye-products being formed. The new substance thus differs markedly from β-β-thioxylene, which is readily oxidised to the known dicarboxylic acid. A. J. G.

Behaviour of Anisoïls at High Temperatures. By E. Bamberger (*Ber.*, **19**, 1818—1821).—These compounds when heated, all suffer decomposition into a phenol and an olefine. β-Naphthyl ethyl ether when heated for 24 hours at 310—320°, is decomposed into β-naphthol and ethylene. Thymyl ethyl ether suffers slight decomposition at 320—330°, and at 360—400° is resolved into thymol and ethylene. Phenetoïl is scarcely altered at 320—340°, but at 380—400° it is split up into phenol and ethylene. Phenyl isobutyl ether decomposes at 380—400° into phenol and butylene. Anisoïl is resolved at 380—400° into phenol and ethylene. A. J. G.

Ortho- and Para-nitranilines from the Corresponding Nitrophenols. By V. Merz and C. Ris (*Ber.*, **19**, 1749—1754).—Orthonitraniline may be readily prepared by heating orthonitrophenol with aqueous ammonia under pressure at 160—170°. The best result is obtained when 20 c.c. of a 35 per cent. aqueous solution of ammonia is used to every 12 grams of nitrophenol; the yield is then 60—70 per cent. of the nitrophenol taken. Paranitraniline may be similarly prepared from paranitrophenol, but the yield is not quite so good. The best results are obtained when 6 grams of the nitrophenol are heated with 20 c.c. of the ammonia solution at 190—200°, when about 55 to 60 per cent. of nitraniline is produced. The above method forms the best means for the preparation of orthonitraniline. Copper must be avoided in the digestors employed, as it is attacked and also diminishes the yield of nitraniline. L. T. T.

Toluidines. By L. Lewy (*Ber.*, **19**, 1717—1719).—When equal molecular proportions of aniline and phosphoric acid are brought together, monaniline phosphate is not formed, but the aniline unites with half the acid to form the salt $(NH_2Ph)_2H_3PO_4$, leaving the other half of the acid free. A solution of this salt, if shaken with aniline, yields crystals of *trianiline phosphate*, $(NH_2Ph)_3H_3PO_4$, but this loses a third of its aniline on exposure to the air. Paratoluidine also forms a *ditoluidine phosphate*, $(C_7H_9N)_2HPO_4$. The ditoluidine salt is very sparingly soluble in cold water, more easily, but with partial dissociation, in boiling water. It crystallises in scales or needles. Orthotoluidine forms a *monotoluidine phosphate*, $(C_7H_9N)H_3PO_4$, but no di- or tri- salt. The monorthotoluidine salt is more easily soluble in water than the diparatoluidine and dianiline salts. A solution of orthotoluidine phosphate when shaken with aniline or paratoluidine yields up all its phosphoric acid to these bases to form di-salts. This reaction forms a good method for the purification of orthotoluidine containing paratoluidine or aniline. The orthotoluidine to be purified is shaken with rather more of a 21 per cent. aqueous solution of phosphoric acid than would be sufficient to form bibasic phosphate with the aniline or paratoluidine believed to be present. These latter bases are entirely precipitated, together with a little monorthotoluidine phosphate. The remaining toluidine is quite pure, containing no paratoluidine that can be detected by Rosenstiehl's reaction. L. T. T.

Reaction of Aniline with Orcinol. By A. Zega and K. Buch (*J. pr. Chem.* [2], **33**, 538—548).—In continuation of experiments on the reaction between phenols and aromatic amines, it is here shown that orcinol forms with aniline either a hydroxyamine or a diamine, according to the conditions of the experiment.

Phenylmetahydroxytolylamine, $OH\cdot C_7H_6\cdot NHPh$, prepared by heating 1 part of orcinol, 2 parts of aniline, and 1 part of calcium chloride at 260—270°, crystallises in colourless thick needles, melts at 79°, and boils at 345°. It dissolves in alcohol, ether, and acetone, but is only sparingly soluble in petroleum. It dissolves without coloration in concentrated sulphuric acid, but on addition of a nitrate a yellow colour is produced. Its hydrochloride is a white crystalline powder. On distillation with zinc-dust, it yields phenylmetatolylamine.

Diphenylmetatoluylenediamine, $C_7H_6(NHPh)_2$, obtained from 1 part of orcinol, 4 parts of aniline, and 2 parts of a mixture of zinc and calcium chlorides, crystallises in white needles, and melts at 105°. It dissolves in alcohol, ether, and benzene, as also in concentrated sulphuric acid without coloration, but on addition of a nitrate a blue-violet colour is produced.

Its *diacetyl-derivative*, $C_7H_6(NAcPh)_2$, crystallises in needles or rhombohedra, melts at 160°, and is moderately soluble in alcohol, ether, and benzene; the *dibenzoyl-derivative*, $C_7H_6(NBzPh)_2$, crystallises in white needles melting at 190°; the *dinitroso-compound*, $C_7H_6(NPhNO)_2$, forms yellow needles; and the *dimethyl-derivative*, $C_7H_6(NPhMe)_2$, white flat crystals moderately soluble in alcohol, ether, and benzene.

V. H. V.

Derivatives of Phenethylamine. By A. Neubert (*Ber.*, **19**, 1822—1826).—*Phenethylthiocarbamide*, $NH_2\cdot CS\cdot NH\cdot CH_2\cdot CH_2Ph$, is obtained by heating phenethylamine hydrochloride in aqueous solution with potassium thiocyanate; it crystallises in white, rhombic plates, melts at 123°, and also under boiling water, and is readily soluble in alcohol and ether.

Phenethylthiohydantoïn hydrochloride, $C_8H_9N:C<\begin{matrix}S\cdot CH_2-\\ NH\cdot CO\end{matrix}>,HCl$, is obtained by heating phenethylthiocarbamide in alcoholic solution with rather more than the equivalent quantity of chloracetic acid. It forms colourless crystals which turn yellow at 165°, brown at 178°, sinter together at 184°, and melt at 188° to a clear red liquid. It is readily soluble in water and hot alcohol, insoluble in ether. On adding potash, the free base separates in white filiform masses.

Diphenethylthiocarbamide, $CS(NH\cdot C_8H_9)_2$, is prepared by boiling phenethylamine with carbon bisulphide in a reflux apparatus until hydrogen sulphide ceases to be evolved. It crystallises in white plates, melts at 84°, and is readily soluble in alcohol and ether. The acetyl-derivative crystallises in colourless prisms, melts at 73°, and is very readily soluble in acetic acid, alcohol, and hot water.

Phenethylthiocarbimide, $C_8H_9\cdot N:CS$, a thick yellow oil, having the odour characteristic of thiocarbimides, is obtained by heating aqueous solutions of mercuric chloride and phenethylamine phenethylthiocarbamate. The latter substance, $C_8H_9\cdot NH\cdot CS\cdot SNH_3\cdot C_8H_9$, is obtained by

the action of carbon bisulphide on phenethylamine; it melts at 128—130°, and yields phenethylthiocarbamic acid when treated with acids.

Ethyl phenethylallophanate, $C_8H_9{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}COOEt$, is prepared by heating an alcoholic solution of phenethylcarbamide with ethyl chlorocarbonate in a reflux apparatus for half an hour. It crystallises in colourless needles, melts at 106°, and is soluble in hot water, alcohol, and ether.

Diphenethyloxamide, $C_2O_2(NH{\cdot}C_8H_9)_2$, obtained by the action of phenethylamine on ethyl oxalate, forms white crystals, melts at 180°, and is readily soluble in alcohol and ether, insoluble in water.

A. J. G.

Acetorthotoluylenediamine and Acetazimidotoluene. By P. Boessneck (*Ber.*, **19**, 1757—1760).—*Acetorthotoluylenediamine*,

$$NH_2{\cdot}C_6H_3Me{\cdot}NHAc\ [Me : NH_2 : NHAc = 1 : 3 : 4],$$

is obtained by moistening metanitroparacetotoluide with water, heating on the water-bath, and then adding a little acetic acid and excess of iron filings. It crystallises in scales melting at 130—131°. It is soluble in boiling water, and in alcohol, ether, and benzene. It oxidises very easily when exposed to the air, and can scarcely be obtained absolutely colourless. The hydrochloride has a reducing action on silver nitrate. When distilled, the base yields Hobrecker's ethenyltoluylene-amidine. When the hydrochloric solution of the diamine is treated with sodium nitrite, *acetazimidotoluene*, C_6H_3Me  NAc

[Me : N : N = 1 : 3 : 4], is formed. This crystallises in large, colourless needles melting at 130·5°, and dissolves in alcohol and glacial acetic acid. It is a very indifferent substance, and is neither soluble in alkalis nor in mineral acids. When boiled with mineral acids, the acetyl-group is split off and azimidotoluene formed. L. T. T.

Chlorazo- and Hydrazo-benzene, and the Behaviour of the Latter towards Acids. By K. Heumann and E. Mentha (*Ber.*, **19**, 1686—1689).—*Parachlorazobenzene*, $NPh : N{\cdot}C_6H_4Cl$, is prepared by heating 100 grams of paramidoazobenzene with 220 c.c. of strong hydrochloric acid and 2 litres of water; when cold, a concentrated solution of 20 grams of sodium nitrite is gradually added. After some time, it is filtered and slowly poured into a boiling solution of 40 grams of cuprous chloride in 360 c.c. of strong hydrochloric acid. The whole is kept boiling for some time, filtered, and the dark coloured mass so obtained is treated successively with strong hydrochloric acid and dilute aqueous soda. It is then extracted with alcohol, and purified by means of animal charcoal. It forms lustrous yellowish-brown plates, readily soluble in hot alcohol, ether, and benzene; it melts at 88—89°, and sublimes in brownish-yellow needles. When warmed with fuming sulphuric acid, it is converted into a monosulphonic acid melting at 148°. Fuming nitric acid converts it into a nitro-compound melting at 132·5°. When the diazoazobenzene chloride is mixed with cuprous chloride kept at −8°, a brown precipitate is formed containing copper (comp. this vol., p. 625).

Chloroparahydrazobenzene, $NHPh{\cdot}NH{\cdot}C_6H_4Cl$, is obtained by treating a solution of chlorazobenzene in alcohol with ammonia and hydrogen sulphide. It forms long white needles melting at 89—90°, insoluble in water, readily soluble in alcohol and ether. It is readily oxidised when exposed to air, and is reconverted into chlorazobenzene. When heated with dilute sulphuric acid, it is converted quantitatively into chlorazobenzene, parachloraniline, and aniline, and thus behaves analogously to paradichlorhydrazobenzene (Calm and Heumann, Abstr., 1880, 880). N. H. M.

Method of Preparing Amidoximes. By F. Tiemann (*Ber.*, **19**, 1668).—Benzenylamidoxime is prepared by boiling an alcoholic solution of equal molecular weights of thiobenzamide and hydroxylamine hydrochloride with the necessary amount of sodium carbonate for 15—18 hours. The alcohol is evaporated, the residue treated with water, and extracted with ether. The oil obtained by distilling off the ether is then treated with hydrochloric acid and evaporated to dryness. The crude hydrochloride is purified by dissolving it in alcohol and precipitating with ether.

Other thioamides can be converted into amidoximes in a similar manner. N. H. M.

Benzenylanilidoxime. By H. Müller (*Ber.*, **19**, 1669—1673).—*Benzenylanilidoxime*, $HO{\cdot}N : CPh{\cdot}NHPh$, is obtained from chlorobenzanilide by Tiemann's method (compare preceding Abstract). It forms slender white needles, soluble in hot water, alcohol, ether, &c.; it melts at 136°. It has acid as well as basic properties, and forms characteristic salts with acids. The *benzoyl-derivative*, $BzON : CPh{\cdot}NHPh$, is prepared by dissolving the amidoxime in benzoic chloride. It forms lustrous, white, matted needles, soluble in alcohol, ether, benzene, &c., insoluble in water and light petroleum. It melts at 116°.

Benzenylphenylimidoximecarbonyl, $CPh\begin{matrix}<^{N{\cdot}O}_{NPh}\end{matrix}>CO$, is obtained by adding ethyl chlorocarbonate diluted with chloroform to a solution of benzenylanilidoxime in chloroform. The mixture is heated for a short time on a water-bath. It crystallises from dilute alcohol in long white needles melting at 166—167°, insoluble in water, readily soluble in alcohol, ether, and benzene.

Benzenyluranilidoxime, $OH{\cdot}N : CPh{\cdot}NPh{\cdot}CO{\cdot}NH_2$, is formed when benzenylanilidoxime is treated with potassium cyanate in aqueous solution. The product is recrystallised from dilute alcohol, from which it separates in yellowish needles melting at 165—167°, soluble in alcohol, benzene, &c., insoluble in water. It is isomeric with Krüger's benzenylphenyluramidoxime (Abstr., 1885, 896).

Benzenylanilidoxime ethyl ether, $OEt{\cdot}N : CPh{\cdot}NHPh$, is prepared by treating benzenylanilidoxime dissolved in absolute alcohol with sodium ethoxide and ethyl iodide. The mixture is heated for some time on a water-bath. It melts at 56°, and soon becomes red when kept. It could not be analysed. N. H. M.

Behaviour of some Aromatic Carbamides at High Temperatures. By A. Barr (*Ber.*, **19**, 1765—1770).—Merz and Weith (*Zeits. f. Chem.*, 1869, 585) found that diphenylcarbamide is decomposed by continuous boiling, large quantities of triphenylguanidine being formed, whilst Hentschel states (Abstr., 1883, 1107) that no decomposition takes place even on repeated distillation. The author has therefore reinvestigated this subject.

Diphenylcarbamide was subjected to continuous boiling in a reflux apparatus, in atmospheres of air, hydrogen, and carbonic anhydride, and also heated in a closed tube. In all cases decomposition took place. In air and hydrogen, 75—85 per cent. of the carbamide was decomposed, 50—60 per cent. triphenylguanidine and 4—8 per cent. aniline formed. In carbonic anhydride and in closed tubes, the reaction was similar, but only about 50—60 per cent. of the carbamide was decomposed. The reaction appears to take place according to the equation $3CO(NHPh)_2 = 2NPh : C(NHPh)_2 + CO_2 + H_2O$. Diparatolylcarbamide undergoes a similar decomposition, yielding triparatolylguanidine and paratoluidine. Diorthotolylcarbamide is decomposed when heated, but the reaction is different from the above: no guanidine is formed, but much toluidine is liberated, and a high boiling oil formed which has not been investigated. L. T. T.

Melting Point and Crystalline Form of Thiocarbanilide. By S. M. Losanitsch (*Ber.*, **19**, 1821—1822).—The melting point of thiocarbanilide is variously stated as 144°—150·5°, most observers giving the lower figure. The author finds a very pure specimen to melt at 151°, and attributes the lower figure generally observed to admixture with the urethane NHPh·CS·OEt. Thiocarbanilide crystallises in the rhombic system; $a : b : c = 0{\cdot}7150 : 1 : 3{\cdot}2597$.

A. J. G.

Oxidation Products of Phenylthiourethane. By P. Jacobson (*Ber.*, **19**, 1811—1813).—When phenylthiourethane is oxidised in hot (80—90°) alkaline solution with potassium ferricyanide, it yields Hofmann's ethoxyphenylthiocarbimide (Abstr., 1880, 388).

Phenylthiourethane sulphide, the chief product of the oxidation when conducted in the cold (this vol., p. 700), is at once and completely converted into phenylthiourethane when heated with alcoholic potash. This behaviour renders it highly probable that it has the formula NPh : C(OEt)·S·S·C(OEt) : NPh. A. J. G.

Action of Potassium Cyanide on Terephthalaldehyde. By H. Oppenheimer (*Ber.*, **19**, 1814—1818).—Grimaux (this Journal, 1877, i, 206) obtained by the action of potassium cyanide on terephthalaldehyde a yellow amorphous substance of the formula $(C_8H_6O_2)_n$, which he regarded as a polymeride of the aldehyde. The author has repeated and confirmed Grimaux's observations, and finds the substance to be *benzoindialdehyde*, $COH·C_6H_4·CH(OH)·CO·C_6H_4·COH$. It reduces ammoniacal silver solutions, gives a yellow compound with phenylhydrazine, and also reduces Fehling's solution when heated. When treated with aqueous soda, it is resolved into terephthalic, benzoindicarboxylic, and a third uninvestigated acid, together with paraxylene

alcohol. When oxidised with chromic mixture, it yields terephthaldehyde and terephthalic acid.

Benzoindicarboxylic acid, $COOH{\cdot}C_6H_4{\cdot}CO{\cdot}CH(OH){\cdot}C_6H_4{\cdot}COOH$, is obtained by oxidising benzoindialdehyde with alkaline permanganate in the cold. It crystallises in short interlaced needles, does not melt, can be sublimed, and is soluble in hot water. It is a polymeride of terephthalaldehydic acid, but the latter is not converted into it by treatment with potassium cyanide.

Hydrobenzoindicarboxylic acid, $C_{16}H_{14}O_6$, is obtained by reducing with sodium amalgam the preceding acid, which it closely resembles in properties, but is distinguished by its greater solubility in water, and in not being sublimable. When heated with hydriodic acid in sealed tubes at 130—140° for some hours, it yields small quantities of dibenzyl. A. J. G.

Action of Hydroxylamine on Diketones. By F. Münchmeyer (*Ber.*, **19**, 1845—1852).—A continuation of the author's researches, showing the inaccuracy of the assumption that diketones containing the group CO·CO yield dioximes, whilst those in which the carbonyl groups are sundered yield monoximes (compare this vol., p. 350). Dibutyril, as already stated, yields only a *monoxime*,

$$Pr^{\alpha}{\cdot}CO{\cdot}CPr^{\alpha}{:}NOH;$$

this is a viscous oil, of odour recalling both ethyl butyrate and quinoline; it can be distilled in small quantity, with but slight decomposition, and is readily soluble in concentrated hydrochloric acid.

Terephthalophenone is conveniently prepared by the action of aluminium chloride on a mixture of terephthalic chloride and benzene. When heated with hydroxylamine hydrochloride and soda, it yields the *dioxime* $C_6H_4(CPh : NOH)_2$ [1 : 4]; this forms white crystals, and melts at 235°. Isophthalophenone, when treated in like manner, also yields a *dioxime*, $C_6H_4(CPh : NOH)_2$ [1 : 3], which forms white crystals, and melts at 70—75°.

Ethyl diacetosuccinate, when treated with excess of an alkaline solution of hydroxylamine, yields the *dioxime*

$$OH{\cdot}N{:}CMe{\cdot}CH(COOEt){\cdot}CH(COOEt){\cdot}CMe{:}N{\cdot}OH;$$

this crystallises in white needles, shows marked acid properties, and decomposes with explosion when heated at 190°. Its lead salt is obtained as a white insoluble precipitate.

Ethyl terephthalyl ketone, $C_6H_4(COEt)_2$, is obtained by the action of zinc ethyl on terephthalic chloride. It crystallises in lustrous white needles, and melts at 220°. It does not react with hydroxylamine, but combines readily with phenylhydrazine.

Tetramethyldiamidobenzophenone is not attacked by free hydroxylamine, but reacts with hydroxylamine hydrochloride to form the *oxime*, $OH{\cdot}N{:}C(C_6H_4{\cdot}NMe_2)$; this is crystalline, and melts at 98—99°. A. J. G.

Meta- and Para-isobutylbenzoic Acids and Isobutylbenzene. By W. Kelbe and G. Pfeiffer (*Ber.*, **19**, 1723—1730).—In a previous

communication (Abstr., 1883, 796), Kelbe showed that metaisobutyltoluene, when oxidised with dilute nitric acid, yields an acid containing the same number of carbon-atoms as the hydrocarbon. The authors have now further investigated this reaction, in order to determine whether the acid formed is an isobutylbenzoic or a tolnylbutyric acid.

Isobutyltoluene was prepared by the action of isobutyl bromide on toluene in the presence of aluminium bromide. The fraction of the product passing over between 140° and 200° was oxidised with dilute (14 per cent.) nitric acid, and the products obtained showed that both meta- and para-isobutyltoluene had been formed.

Para-isobutylbenzoic acid, $C_4H_9 \cdot C_6H_4 \cdot COOH$, forms monoclinic crystals, melting at 164°. The *silver salt* is amorphous; the *amide* forms long thin needles, melting at 171°, and soluble in boiling water. *Nitropara-isobutylbenzoic acid* crystallises from water in long thin needles, melting at 161°. Its *silver salt* is white; its *methyl salt* is liquid. When heated with dilute nitric acid, para-isobutylbenzoic acid yields terephthalic acid.

Meta-isobutylbenzoic acid crystallises from light petroleum in long broad needles, melting at 127°. The *silver salt* is white, and slightly soluble in water; the *amide* crystallises from water in hair-like needles, melting at 130°. *Nitrometa-isobutylbenzoic acid* crystallises from light petroleum in small needles, and melts at 140°. Its *silver salt* is slightly soluble in water; its *methyl salt* is liquid. When heated with dilute nitric acid, meta-isobutylbenzoic acid yields isophthalic acid.

Both the meta- and para- acids, when heated with excess of lime, yield isobutylbenzene (b. p. 166°), showing that they are benzoic, and not butyric acids. It is thus proved that in these cases at least the usual rule does not hold good, that in the oxidation of homologues of toluene containing two side-chains, the larger chain is first attacked.

Isobutylbenzenesulphonic acid was prepared by dissolving the above isobutylbenzene in fuming sulphuric acid. The *barium* and *potassium salts* form scales, the *amide* glistening needles melting at 137°.

Isobutylbenzene is not easily oxidised, requiring to be heated at 180—200° with nitric acid, when it forms benzoic acid. This difficulty in oxidising the isobutyl-group probably determines the oxidation of the methyl-group in isobutyltoluene.

Attempts to prepare ortho-isobutyltoluene proved unsuccessful.

L. T. T.

Compounds of Phenyl Mercaptan with Ketonic Acids. By R. Escales and E. Baumann (*Ber.*, **19**, 1787—1796).—*α-Dithiophenylpropionic acid*, $CMe(SPh)_2 \cdot COOH$, is obtained by treating the additive product of phenyl mercaptan and pyruvic acid (Abstr., 1885, 513) with hydrogen chloride at 100°, or even by heating it alone at 100°. It crystallises in stellate groups of needles, melts at 116—117°, and is decomposed into mercaptan and uncrystallisable products at higher temperatures; it is insoluble in water, readily soluble in alcohol, ether, and benzene, more sparingly in light petroleum. It is not decomposed when boiled with aqueous or alcoholic potash, ammonia, or hydro-

chloric acid. Alcoholic ammonia at 200° decomposes it into mercaptan and phenyl disulphide. The sodium and barium salts are described. The *ethyl* salt is a viscous oil, heavier than water; it cannot be distilled without decomposition. The *chloride* is liquid; the *amide*, $C_{15}H_{13}S_2O{\cdot}NH_2$, crystallises in thick needles or prisms, and melts at 92—93°.

Dithiophenylphenylacetic acid, $CPh(SPh)_2{\cdot}COOH$, is obtained by the action of hydrogen chloride on the compound of phenyl mercaptan and benzoylformic acid (Abstr., 1885, 750). It melts at 143°, and loses mercaptan on further heating, is insoluble in water, sparingly soluble in benzene and light petroleum, readily soluble in ether, alcohol, chloroform, and acetic acid. The potassium salt is described.

Ethyl β-dithiophenylbutyrate, $CMe(SPh)_2{\cdot}CH_2{\cdot}COOEt$, is obtained by the action of hydrogen chloride on a mixture of phenyl mercaptan (2 mols.) and ethyl acetoacetate (1 mol.). It crystallises in nacreous plates or large transparent prisms, melts at 57—58°, and is in part converted into uncrystallisable products when heated for some time at 100°; it is readily soluble in ether, benzene, and chloroform, sparingly in light petroleum, acetic acid, and cold alcohol, insoluble in water, and gives a cherry-red coloration with concentrated sulphuric acid. The free acid could not be obtained, as the ethyl salt when treated with alkalis is decomposed into phenyl mercaptan and *β-thiophenylcrotonic acid*, $SPh{\cdot}CMe : CH{\cdot}COOH$. The latter crystallises in large tables, melts at 176—177° with evolution of carbonic anhydride, is insoluble in cold water, readily soluble in benzene, light petroleum, and hot alcohol. When boiled for some time with aqueous potash, the acid is in part decomposed into phenyl mercaptan, acetone, and (?) tetrolic acid. Bromine attacks it, forming an indifferent crystalline bromo-compound; carbonic anhydride is at the same time evolved. Whether an isomeric acid is formed at the same time as β-thiophenylcrotonic acid is left uncertain.

Thiophenylpropylene, $C_3H_5{\cdot}SPh$, is obtained together with carbonic anhydride by heating β-thiophenylcrotonic acid above its melting point; it is a colourless oil, of peculiar ethereal odour, boils at 206—210°, volatilises with steam, and gives with sulphuric acid a blue coloration, turning dirty violet on heating. When treated with bromine, it yields the same compound as is obtained by the action of bromine on β-thiophenylcrotonic acid.

γ-Dithiophenylvaleric acid, $CMe(SPh)_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is formed by the action of hydrogen chloride on a mixture of levulinic acid and phenyl mercaptan. It crystallises in strongly refractive lustrous prisms, melts at 68—69°, and is readily soluble in alcohol, ether, benzene, and chloroform, sparingly in light petroleum, insoluble in water. When heated with acids, it is readily decomposed into levulinic acid and phenyl mercaptan. A. J. G.

Action of Potassium Cyanide on Lactones. By W. Wislicenus (*Annalen*, **233**, 101—116).—The formation of benzyl cyanide orthocarboxylic acid by the action of potassium cyanide on phthalide at 180°, the properties of this acid and of its product of decomposition, phenylacetorthocarboxylic acid, have been previously described by

the author (Abstr., 1885, 532). Phenylacetorthocarboxylic acid melts at 175°, and is identical with the *isuvitic* acid of Barth and Hlasiwetz (*Annalen*, **138**, 68).

If the mixture of potassium cyanide and phthalide is heated at 190—200°, the product is insoluble in water. It dissolves in hot glacial acetic acid, and the liquid, on cooling, deposits a crystalline acid of the composition $C_{18}H_{14}N_2O_3$, or $C_{18}H_{12}N_2O_3$. This acid melts about 240° with decomposition, is insoluble in ether and benzene, and has a bitter taste.

γ-Cyanovaleric acid is formed by the action of potassium cyanide on valerolactone at 290°. It crystallises in small prisms melting at 95°, and is soluble in water, benzene, and chloroform. It yields α-methylglutaric acid on hydrolysis. W. C. W.

Thiocoumarin and its Derivatives. By F. Tiemann (*Ber.*, **19**, 1661—1667).—*Thiocoumarin*, $C_6H_4<\begin{matrix}CH:CH\\ -O\cdot CS-\end{matrix}>$, is prepared by heating a mixture of powdered coumarin and phosphorus pentasulphide at 120°; the product is powdered, repeatedly extracted with benzene, and the residue obtained by evaporating the benzene is boiled with dilute alcohol. It forms long gold-coloured needles, melting at 101°, insoluble in water, readily soluble in alcohol, ether, and benzene. It sublimes unchanged. It can also be obtained by fusing together orthocoumaric acid and phosphorus pentasulphide. When a solution in dilute alcohol is warmed with caustic potash, and then treated with hydrochloric acid, pure coumarin is obtained.

Coumaroxime, $C_6H_4<\begin{matrix}CH:CH\\ O\text{———}\end{matrix}>C:N\cdot OH$, is formed by the action of free hydroxylamine on thiocoumarin. It crystallises from boiling water in long white needles, melting at 131°; it dissolves readily in alcohol, benzene, and ether; also in acids and alkalis. Prolonged heating with hydrochloric acid decomposes it into coumarin and hydroxylamine hydrochloride. The *ethyl ether*, $C_9H_6O:N\cdot OEt$, is prepared by the action of sodium ethoxide and ethyl iodide on coumaroxime. It forms nearly colourless plates, readily soluble in alcohol, &c., insoluble in water; it melts at 50°.

Dihydrocoumaroxime, $C_6H_4<\begin{matrix}CH_2\cdot CH_2\\ O\text{———}\end{matrix}>C:N\cdot OH$, is obtained by reducing coumaroxime with sodium amalgam.

The *phenylhydrazine-derivative* of coumarin, $C_{15}H_{12}N_2O$, forms long gold-coloured needles, soluble in hot alcohol, readily in ether and benzene; it melts at 143—144°.

Aniline reacts with thiocoumarin, with formation of a very unstable compound, which could not be isolated. N. H. M.

Derivatives of Umbelliferone. By W. Will and P. Beck (*Ber.*, **19**, 1777—1786).—In a previous paper (Abstr., 1884, 68), the author has described two isomeric (α- and β-) *dimethylumbellic acids*. The best method to prepare the α- or unstable acid is to enclose a mixture of 4 grams of potash dissolved in 50 c.c. methyl alcohol, 5 grams

umbelliferone methyl ether, and 10 grams methyl iodide in a tube, and allow the mixture to remain, with frequent shakings, for 12—18 hours. In this way the α-acid, melting at 138°, is alone produced. It forms white crystals, soluble in alcohol. The *barium salt* crystallises in well-formed, concentrically grouped needles; the *calcium salt* forms white crystals. *Umbelliferone ethyl ether*,

$$EtO\cdot C_6H_3<\begin{matrix}CH:CH\\ -O\cdot CO-\end{matrix}> [CH:O:OEt = 1:2:4],$$

is produced when equal molecular proportions of umbelliferone, potash, and ethyl iodide are heated together in alcoholic solution. It crystallises in slightly reddish scales, which melt at 88°, and are readily soluble in alcohol, ether, benzene, and glacial acetic acid, but almost insoluble in water. It is soluble in hot alkalis and carbonated alkalis, but is reprecipitated unchanged as these solutions cool. Like the methyl ether, it yields two isomeric diethylated acids. *α-Diethylumbellic acid*, $C_6H_3(OEt)_2\cdot CH:CH\cdot COOH$, crystallises in small glistening scales, melting at 106·5°, and soluble in alcohol, ether, and benzene. It is less easily converted into the β-acid than the corresponding methyl acid, and a temperature of 100° may therefore be used in its preparation. *β-Diethylumbellic acid* is obtained when the foregoing methylation is carried out at 150°. It forms white shining crystals, melting at 200°, is sparingly soluble in boiling water, but easily in alcohol and ether. It may also be prepared directly from the α-acid by boiling the latter. Slight decomposition takes place, and on cooling the acid is found to have changed into the β-modification.

Bromumbelliferone methyl ether, $C_6H_3(OMe)<\begin{matrix}CH:CBr\\ -O-CO-\end{matrix}>$, is obtained by adding bromine to a solution of the ether in carbon bisulphide. It crystallises in long white needles, melts at 154—154·5°, is soluble in boiling alcohol and ether, very sparingly in boiling water. When heated, it has an odour resembling that of coumarin; and when boiled with alcoholic potash, it forms *paramethoxycoumarilic acid*,

$$MeO\cdot C_6H_3<\begin{matrix}CH\\ -O-\end{matrix}>C\cdot COOH.$$

This acid forms long white needles, soluble in alcohol and ether, sparingly in water, and melts at 195·5—196·5°. Its *barium salt*, $(C_{10}H_7O_4)_2 + 4H_2O$, forms white crystals. When treated with sodium amalgam, the acid yields *paramethoxyhydrocoumarilic acid*,

$$MeO\cdot C_6H_3<\begin{matrix}CH_2\\ -O-\end{matrix}>CH\cdot COOH,$$

crystallising in columns melting at 114°, and soluble in the usual solvents. It is volatile in steam. *Paramethoxycoumarone*,

$$MeO\cdot C_6H_3<\begin{matrix}CH\\ -O-\end{matrix}>CH,$$

was obtained by heating silver paramethoxycoumarilate in a current of carbonic anhydride. It is a colourless oil, heavier than water,

and boils at 178—180°. It is insoluble in alkalis, easily soluble in alcohol and ether. It is volatile in steam, and has an intense and pleasant odour.

Bromumbelliferone ethyl ether forms silvery plates, melting at 115·5°, easily soluble in boiling alcohol and in ether. A dilute alcoholic solution has a strong violet fluorescence. *Para-ethoxycoumarilic acid*, $EtO\cdot C_6H_3<\begin{matrix}CH\\-O-\end{matrix}>C\cdot COOH$, forms glistening needles, melting at 162—163°. *Para-ethoxyhydrocoumarilic acid* crystallises in hard white needles, melting at 119°.

Dibromumbelliferone methyl ether, $MeO\cdot C_6H_2Br<\begin{matrix}CH:CBr\\-O-CO-\end{matrix}>$, is obtained by adding an excess of bromine to a solution of the ether in glacial acetic acid. It melts at 249—251°, and forms white glistening needles, sparingly soluble in alcohol. The corresponding *ethyl ether* melts at 216°, and closely resembles the methyl compound. It is probable that one bromine-atom in these compounds is present in the benzene-ring.

This research shows that the umbelliferone ethers are true coumarins, and, like the latter, yield two isomeric alkyloxy-acids.

L. T. T.

Diphthalyl. By C. Graebe and P. Guye (*Annalen*, **233**, 241—248).—The best yield of diphthalyl is obtained by heating a mixture of phthalide (1 part), phthalic anhydride (2 parts), and powdered anhydrous sodium acetate (½ part), for 10 hours at 260—265°. The product is extracted with hot water, and the residue dissolved in alcohol. The crystals deposited from this alcoholic solution may be further purified by recrystallisation from glacial acetic acid.

If thiophthalic anhydride is substituted for phthalic anhydride, the formation of diphthalyl takes place more readily, but this process is not of any practical value owing to the difficulty of preparing thiophthalic acid.

Nitrodiphthalyl, $<\begin{matrix}C_6H_4\\CO\cdot O\end{matrix}>C:C<\begin{matrix}C_6H_3(NO_2)\\O\text{——}CO\end{matrix}>$, is prepared by heating a mixture of nitrophthalide, phthalic anhydride, and sodium acetate at 230° for eight hours. Nitrodiphthalyl is less soluble than diphthalyl. It is deposited from glacial acetic acid in yellow needles melting at 270°. It unites directly with 2 atoms of bromine, forming a dibromide which melts with decomposition at 210°. It is also decomposed by alcoholic potash, forming an acid, probably nitrodiphthalic acid.

Hydroxydiphthalyl is formed by the action of phthalic anhydride on β-hydroxyphthalic acid in presence of sodium acetate. It crystallises from glacial acetic acid in needles. This substance begins to decompose at 374° without melting.

Tetrachlorodiphthalyl, $<\begin{matrix}C_6H_4\\CO\cdot O\end{matrix}>C:C<\begin{matrix}C_6Cl_4\\O\cdot CO\end{matrix}>$, is prepared by boiling for four hours a mixture of tetrachlorophthalide (2 parts) and phthalic anhydride (1 part). The product is extracted with boiling acetic acid, and the residue is dissolved in phenol; the tetrachlorodiphthalyl is precipitated on the addition of alcohol to this solution.

It dissolves freely in chloroform, aniline, and phenol. It is decomposed by heat without melting.

Diphthalylimide, $C_{16}H_9NO_3$, can be prepared by the condensation of phthalic anhydride and phthalimidine, $C_8H_4O_3 + C_8H_7NO = C_{16}H_9NO_3 + H_2O$, by the action of phthalimide on phthalimidine,

$$C_8H_5NO_2 + C_8H_7NO = C_{16}H_9NO_3 + NH_3,$$

and by gently boiling a mixture of phthalide and phthalimde,

$$C_8H_6O_2 + C_8H_5NO_2 = C_{16}H_9NO_3 + H_2O.$$

Diphthalylimide is identical with the substance which Graebe and Schmalzigaug obtained (Abstr., 1885, 798) on warming diphthalyllactonic acid and ammonia. W. C. W.

Lactones. By V. Meyer and F. Münchmeyer (*Ber.*, **19**, 1706—1708).—When phthalide is warmed with phenylhydrazine for some hours on a water-bath, the two combine with elimination of 1 mol. of water, and yield the compound $C_{14}H_{12}ON_2$. The latter forms lustrous needles melting at 175°. The authors intend to investigate the behaviour of phenylhydrazine towards other classes of oxygen compounds, and consider in the meantime that there is not yet sufficient evidence to show that phenylhydrazine and hydroxylamine are identical in their reactions; and further, that the fact that an aromatic dioxide combines with phenylhydrazine is not sufficient evidence to show that it is an aldehyde or ketone, as it might also be a lactone. N. H. M.

Phenylbenzenesulphonate. By R. Otto (*Ber.*, **19**, 1832—1835. Compare Abstr., 1878, 414). — *Phenylbenzenesulphonate*, $PhSO_2OPh$, is obtained by the action of sodium phenoxide on benzenesulphonic chloride. It crystallises in rhombic forms; $a : b : c = 0{\cdot}7847 : 1 : 0{\cdot}8576$; observed faces, $\infty\breve{P}\infty$, $\infty\breve{P}\infty$, ∞P, $\breve{P}\infty$. It melts at 34—35°, and is readily soluble in benzene, ether, and alcohol, insoluble in water. It is saponified, although not very readily, when boiled with potash; alcoholic ammonia at 200° does not attack it.

Phenylparatoluenesulphonate, $C_6H_4Me{\cdot}SO_3Ph$, prepared in like manner from paratoluenesulphonic chloride, crystallises in lustrous, white, rhombic needles; $a : b : c = 0{\cdot}2894 : 1 : 0{\cdot}4759$; observed faces, $\infty\breve{P}\infty$, $\infty\breve{P}\infty$, $\infty\breve{P}$, $\breve{P}\infty$. It melts at 94—95°, and resembles the benzenesulphonate in solubility and properties. Potassium paratoluenesulphonate crystallises in rhombic forms; $a : b : c = 0{\cdot}8639 : 1 : 3{\cdot}2372$. The chloride crystallises in the asymmetric system; $a : b : c = 0{\cdot}7682 : 1 : 1{\cdot}1139$; $\alpha = 97° 24'$; $\beta = 117° 6'$; $\gamma = 84° 28'$; observed faces, $\infty\breve{P}$, $\infty\breve{P}\infty$, $0P$, ∞P_1, and $\breve{P}_1\infty$. A. J. G.

Action of Alkaline Sulphonates on Salts of Dihalogenated Fatty Acids. By R. Otto and H. Engelhardt (*Ber.*, **19**, 1835—1838).—When sodium dichloracetate (1 mol.) in aqueous solution is heated on the water-bath with sodium benzenesulphinate (2 mols.), only one molecule of the latter salt enters into reaction, as represented in the equation $CHCl_2{\cdot}COONa + PhSO_2Na + H_2O = CH_2Cl{\cdot}SO_2Ph +$

$NaCl + HNaCO_3$, a chlorinated phenylsulphonacetic acid seemingly not being able to exist. Sodium dichloracetate and paratoluenesulphinate do not react under like conditions.

The authors have repeated Michael and Palmer's experiments on iodomethylphenylsulphone (Abstr., 1885, 536) and, whilst confirming the statements made as to its reaction with sodium ethoxide, find that it does not yield methylphenylsulphone when treated with sodium benzenesulphinite.

When sodium benzenesulphinate and α-dichloropropionate react in aqueous solution, ethylenediphenylsulphone is invariably formed notwithstanding variations in the proportions of the ingredients.

A. J. G.

Action of Bromine on Paracymenesulphonic Acid. By W. Kelbe and M. Koschnitzky (*Ber.*, **19**, 1730—1733).—When bromine is added to a solution of paracymenesulphonic acid [Me : Pr : SO_3H = 1 : 4 : 2] at 40—50°, *β-bromocymenesulphonic acid* [Me : Br : Pr : SO_3H = 1 : 3 : 4 : 2] is formed together with a heavy oil. The acid was not prepared in the free state. The *potassium salt* crystallises with 1 mol. H_2O, in colourless needles, the *copper salt* with $12H_2O$ in pale blue needles. The *amide* crystallises from dilute alcohol in needles which melt at 152°. When the potassium salt is saponified, a bromocymene distils over. This is a colourless oil which boils at 225°, and when oxidised with nitric acid at 150° yields an acid crystallising in scales melting at 196°. This is not the bromoparatoluic acid obtained by the oxidation of ordinary bromocymene, and must therefore have the formula $C_6H_3MeBr{\cdot}COOH$ [Me : Br : COOH = 1 : 3 : 4], and the bromocymene must be identical with that obtained by v. Gerichten from thymol, and have the constitution [Me : Br : Pr = 1 : 2 : 3].

The heavy oil formed during the preparation of the β-bromosulphonic acid may be separated by distillation with steam into a volatile and a non-volatile fraction; the latter has not yet been investigated. The volatile fraction is a pale yellow oil having the odour of ordinary bromocymene. It dissolves in fuming sulphuric acid to form *α-bromocymenesulphonic acid*, which yields a *calcium salt* crystallising with $8H_2O$ in long easily soluble needles; a *potassium salt*, with $3H_2O$, forming long needles; a *copper salt* crystallising with $8H_2O$, in bluish-white needles; and an *amide* crystallising in needles which melt at 187·5°. When reduced with ammonia and zinc-dust, the acid yields a *cymenesulphonic acid* giving an *amide* which melts at 145°. This acid is not the one already known, and has therefore the constitution [Me : Pr : SO_3H = 1 : 4 : 3], and the constitution of its bromo-derivative must be [Me : Pr : Br : SO_3H = 1 : 4 : 2 : 5].

L. T. T.

Aromatic Antimony Compounds. By A. Michaelis and A. Reese (*Annalen*, **233**, 39—60).—After referring to the various researches on organic antimony compounds by Loewig and Schweitzer (*Annalen*, **75**, 315), Hofmann (*ibid.*, **108**, 357), Landolt (*ibid.*, **78**, 91, **84**, 44), Buckton (this Journal, 1860, 115) and others, the authors describe the preparation of triphenylstibine by the action of sodium on a solution of antimony trichloride and chlorobenzene in benzene.

The product of the reaction is filtered, the residue repeatedly extracted with benzene, and the extract added to the original filtrate; on evaporation, triphenylstibine mixed with triphenylstibine chloride is deposited. The product is purified by treatment with alcohol mixed with strong hydrochloric acid, the residue being washed with alcohol, dried and transferred to a flask containing light petroleum. Chlorine is passed over the surface of the solution until no further precipitate is produced, and the precipitate is then washed with petroleum and recrystallised from boiling alcohol. The chloride thus obtained is dissolved in alcoholic ammonia, treated with sulphuretted hydrogen, and the precipitated stibine dried and recrystallised from a mixture of alcohol and ether.

Triphenylstibine, $SbPh_3$, forms colourless triclinic plates, which are highly refractive; $a:b:c = 0{\cdot}69695:1:0{\cdot}88938$; $\alpha = 100°\ 37'\ 50''$; $\beta = 103°\ 36'\ 50''$; $\gamma = 75°\ 25'\ 0''$; sp. gr. = 1·4498 at 12°. It is freely soluble in ether, benzene, glacial acetic acid, light petroleum, carbon bisulphide, and chloroform. It melts at 48°, and boils at 360° with slight decomposition. Tripenylstibine unites directly with chlorine, bromine, and certain metallic chlorides, for instance cupric chloride. It decomposes mercuric chloride, forming antimony trichloride and mercuric phenyl chloride. Triphenylstibine readily dissolves in strong nitric acid, and the solution deposits crystals of triphenylstibine nitrate, $Ph_3Sb(NO_3)_2$ (m.p. 156°).

The *dichloride*, Ph_3SbCl_2, forms long slender needles, melts at 143°, and is soluble in benzene and carbon bisulphide. It is not decomposed by water, and is slowly acted on by aqueous solutions of alkalis. Alcoholic potash converts it into the hydroxide.

The *dibromide* is prepared by adding bromine to a solution of triphenylstibine in glacial acetic acid. It melts at 216°, and dissolves freely in benzene, carbon bisulphide, and hot acetic acid. The *iodide*, Ph_3SbI_2, crystallises in glistening tables; it melts at 153°, and dissolves freely in benzene. The *hydroxide*, $Ph_3Sb(OH)_2$, melts at 212°; it is soluble in alcohol.

When a mixture of triphenylstibine and methyl iodide is heated at 200°, a brick-red powder is produced, which appears to be identical with the polymeric modification of trimethylstibine iodide observed by Landolt (*J. pr. Chem.*, **84**, 336). Attempts to prepare zinc phenyl by the action of pure zinc methyl on triphenylstibine were unsuccessful.

In the preparation of triphenylstibine, *diphenylstibine chloride*, Ph_2SbCl_3, is obtained as a bye-product. The yield may be increased by diminishing the quantity of sodium used in the reaction. The crude product is extracted with alcohol mixed with hydrochloric acid, and the residue left on evaporating this extract is repeatedly boiled in dilute hydrochloric acid; on cooling, the solution deposits needle-shaped crystals of the chloride containing 1 mol. H_2O. Diphenylstibine chloride melts at 180°; it is insoluble in water.

Diphenylstibic acid, $Ph_2SbO{\cdot}OH$, is obtained as a white precipitate when ammonia is added to an alcoholic solution of the chloride. The acid dissolves in acetic acid, and in sodium hydroxide solution.

W. C. W.

Preparation of Indole from Orthotoluidine-derivatives. By J. Mauthner and W. Suida (*Monatsh. Chem.*, **7**, 230—240).—*Ethyleneditolyldiamine*, $C_{16}H_{20}N_2$, is prepared by acting on ethylene bromide (1 mol.) with orthotoluidine (2 mols.), treating the resulting mass with potash, and extracting the oil with ether. When purified by conversion into the sulphate and subsequent decomposition, it crystallises from light petroleum in large rhombic tables, melting at 75—76°. Strong nitric acid gives a deep purple-red and iron chloride a deep-brown coloration with the base. Ethyleneditolyldiamine heated with zinc-dust yields indole.

Diethyleneditolyldiamine, $C_{18}H_{22}N_2$, is obtained together with the preceding compound, from which it is separated by its more sparing solubility in alcohol; it forms colourless needles, melting at 170—171°. Its solution gives no precipitate with sodium nitrite. By distillation with zinc-dust, it yields indole.

Oxalorthotoluide, $C_{16}H_{16}N_2O_2$, prepared by heating orthotoluidine with ethyl oxalate, treatment with hydrochloric acid, and crystallisation from hot alcohol, forms white scales melting at 188—190°. It resembles oxanilide in its properties. When treated with zinc-dust, it gives indole.

Oxalorthotoluidic acid, $C_9H_9NO_3 + H_2O$, is prepared by heating potassium ethyl oxalate with orthotoluidine at 180—190°; the mass is treated with water, filtered, decomposed with sulphuric acid, and the precipitated acid recrystallised from hot water. It forms slender colourless needles containing 1 mol. H_2O, which is lost over sulphuric acid in a vacuum. The anhydrous acid softens at 130°, and melts at a higher temperature with decomposition. It is soluble in hot water and alcohol, sparingly in ether and chloroform. With strong nitric acid, it gives a red coloration. The *potassium*, *calcium*, *barium*, and *silver* salts are described. Heated with zinc-dust, the acid yields indole. The best results are obtained when the potassium salt is submitted to dry distillation. The barium salt yields *diorthotolylcarbamide* on dry distillation.

A small quantity of indole is directly formed in the preparation of oxalorthotoluidic acid. G. H. M.

Synthesis of Mixed Azo-dyes from Aromatic Diamines. By M. Lange (*Ber.*, **19**, 1697—1700).—When an excess of benzidine sulphate is added to a definite quantity of strongly acid sodium nitrite solution and the solution afterwards filtered, treated with sodium carbonate, and then with an amount of sodium naphthionate corresponding with half of the amount of nitrite used, an insoluble compound separates; this was found to be the anhydride of a diazoazosulphonic acid, $C_6H_4<\begin{matrix}N_2\cdot SO_3\\ C_6H_4\cdot N_2\end{matrix}>C_{10}H_6\cdot NH_2$. The latter is almost insoluble in water, and is not dissolved by alkaline carbonates. Boiling water converts it into the corresponding hydroxy-compound. When boiled with alcohol, the diazo-group is replaced by hydrogen. Both these derivatives are dyes. When the diazo-compound is added to an alkaline solution of a phenolamine or phenolsulphonic acid, diazo-dyes are at once formed. If the solution of the amine or phenol

contains alkali carbonate instead of free alkali, compounds are formed with evolution of carbonic anhydride which have the properties of strong acids: for example,

$$OH\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot C_6H_4\cdot N_2\cdot C_{10}H_5(NH_2)\cdot SO_3Na.$$

A number of these dyes have been prepared and are of great technical value.

Carboxylic and sulphonic acids of the phenols behave in a similar manner towards tetrazodiphenyl as does naphthionic acid.

N. H. M.

A New Class of Azo-colouring Matters. By C. A. Martius (*Ber.*, **19**, 1755—1756).—The author points out that he and his fellow workers have for some time known of the reactions described by Lange (preceding Abstract), and that several patents have already been taken out with relation to them.

Tetrazo-diphenyl, tetrazo-ditolyl, and tetrazo-dixylyl salts act readily on amines and phenols, or their sulphonic or carboxylic acids. The first reaction takes place between one molecule of the tetrazo-compound and one molecule of the amine or phenol, but the product thus formed is capable of reacting with another molecule of the same or of a different phenol or amine to form a bi-azo-colouring matter. In this way mixed or unsymmetrical azo-compounds of the general formula $R''\cdot N_2\cdot R\cdot R\cdot N_2\cdot R'''$ may be formed where R is phenyl, tolyl, or xylyl, R″ and R‴ identical or different aromatic hydrocarbon or substituted radicles.

L. T. T.

New Synthesis of Triphenylmethane. By H. Griepentrog (*Ber.*, **19**, 1876—1877).—Triphenylmethane is obtained by heating a mixture of 80 grams benzaldehyde, 114 grams benzene, and 80 grams of zinc chloride in sealed tubes at 250—270° for 6—8 hours. It is accompanied by a liquid hydrocarbon. In similar manner benzaldehyde and toluene react with formation of a mixture of isomeric ditolylphenylmethanes.

A. J G.

Action of Primary Aromatic Amines on Benzoïn. By K. Voigt (*J. pr. Chem.* [2], **34**, 1—27).—Benzoïn (phenylhydroxybenzoylketone) was heated for 3—4 hours at 200° in a sealed tube with a slight excess of aniline: the thick oily product, when mixed with alcohol, crystallised at once, and was purified by repeated crystallisation from alcohol. It forms yellow needles, which melt at 99°, and solidify to a transparent glass on cooling. Analysis showed the new substance to be *anilbenzoïn*, to which the author assigns the formula NPh·CPh·CHPh·OH, as best explaining the facts that it gives no phenylhydrazine-compound, and that after reduction with hydrogen it does not yield aniline to mineral acids. Anilbenzoïn has feeble basic properties, and forms a sulphate with dilute sulphuric acid, which is decomposed at once by water; by long continued heating with mineral acids, aniline is separated. Treated with sodium nitrite and hydrochloric acid, yellow needles of the nitroso-compound were obtained, melting with decomposition at 140°. As benzoïn yields no nitroso-derivative, the addition of NO probably occurs in the aniline group. When heated with acetic anhydride, acetylbenzoïn was

readily obtained as a white crystalline mass, melting at 153°; attempts to prepare the same substance directly by heating together acetylbenzoïn and aniline failed.

Bromanilbenzoïn, $C_{20}H_{16}BrNO$, was obtained by the action of bromine on an ethereal solution of anilbenzoïn; it was purified by repeated crystallisation from acetone, when it formed small yellow prisms melting at 167—168°.

When heated with dry zinc-dust, anilbenzoïn is decomposed chiefly into aniline and benzaldehyde, with a small quantity of desoxybenzoïn; the latter substance is also formed on reduction with zinc and acetic acid. With an alcoholic solution of anilbenzoïn, sodium amalgam yields hydrobenzoïnanilide, NHPh·CHPh·CHPh·OH, crystallising from alcohol as a cake of white needles, melting at 119°. This substance shows more marked basic properties than anilbenzoïn, and with dilute sulphuric acid yields a sulphate melting at 175°, and requiring boiling water for its decomposition. On further heating with mineral acids, aniline is not eliminated, but a colourless oil free from nitrogen is obtained.

Paratoluidine acts with benzoïn in the same way as aniline; the compound produced, *paratolilbenzoïn*, forms long yellow needles, melting at 144°, and is sparingly soluble in boiling alcohol. Nitrous acid transforms it into a nitroso-derivative, and with mineral acids, except nitric, it behaves in the same way as the aniline compound. Nitric acid, however, of sp. gr. 1·2, transforms it successively into the mono- and dinitro-derivatives, of which the first crystallises from acetone in fine red prisms, melting at 153°, and the second in yellow masses, melting at 195°. Substitution takes place in both cases in the benzene-ring of the aniline-group. Paratolilbenzoïn, when treated with sodium amalgam, yields the corresponding *hydro-compound* in white needles, melting at 140°, and exhibiting in other respects the same properties as the hydro-derivative of anilbenzoïn.

β-Naphthylamine also yields a similar compound when heated with benzoïn; this substance, *β-naphtilbenzoïn*, crystallises in yellowish prisms, melting at 130°, and yields a nitroso-derivative.

Aniline was found to produce with benzil a compound similar to that produced with benzoïn, namely, NPh : CPh·COPh, in yellow prisms, melting at 105°, and behaving with mineral acids in the same way as anilbenzoïn. J. K. C.

Isobenzil and the Action of Sunlight on some Organic Compounds. By H. Klinger (*Ber.*, **19**, 1862—1870).—Isobenzil crystallises in the monosymmetric system, $a : b : c = 0{\cdot}96083 : 1 : 0{\cdot}82579$; $\beta = 79°\ 59'\ 40''$. When treated with alcoholic potash, it behaves similarly to benzil, gives a violet coloration, and yields a mixture of benzilic and benzoic acids. Nitric acid converts it into benzil and benzoic acid, or nitro-derivatives thereof.

When an ethereal solution of benzil is exposed to direct sunlight, crystals of *benzilbenzoïn*, $C_{42}H_{32}O_6$, separate, as much as 46 per cent. of the benzil having been converted into this substance. The presence of water in the ether is essential; the change does not occur in the dark, and only very partially in diffused daylight. Benzilbenzoïn

crystallises in stellate groups of needles, and melts at 134—135°, being at the same time converted into benzil and benzoïn; the same resolution is more or less speedily effected on treating it with solvents, especially benzene and alcohol. When boiled with potash, it seems to be first resolved into benzoïn and benzil, the latter being then converted into benzilic and benzoic acids; benzoïn also undergoes this latter change if air have access to the liquid.

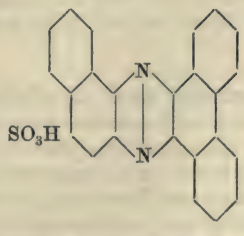
When a solution of phenanthraquinone in moist ether is exposed to direct sunlight, phenanthraquinol and acetaldehyde are formed, the reaction being expressed by the equation $2C_{14}H_8O_2 + Et_2O + H_2O = 2C_{14}H_8(OH)_2 + 2CH_3{\cdot}CHO$. A. J. G.

Constitution of Naphthionic Acid and of Congo-red. By O. N. Witt (*Ber.*, **19**, 1719—1722).—If Cléve's formula for naphthionic acid, $NH_2{\cdot}C_{10}H_6{\cdot}SO_3H$ [$NH_2 : SO_3H = 1 : 4$], is correct, the introduction of an azo-group would take place in the ortho [or 1 : 2] position to the amido-group, whereas if the sulphonic group had any other position the azo-group would take the para (or 1 : 4) position to the amido-group. An ortho-azo-derivative would yield on reduction a sulphonated orthodiamine, which in its turn might be easily converted into a quinoxaline.

Congo-red (the product of the reaction of tetrazodiphenyl chloride on naphthionic acid) when reduced in ammoniacal solution with zinc-dust, yields benzidine and a colourless diamidonaphthalenesulphonic acid. The latter is very unstable and was therefore not purified, but was at once treated with phenanthraquinone and hydrogen sodium sulphite. *Sodium diphenylenenaphthaquinoxalinesulphonate*,

$$C_{24}H_{13}N_2{\cdot}SO_3Na,$$

thus obtained crystallises in lemon-yellow needles having a greenish-grey fluorescence. It is soluble in absolutely pure boiling water or dilute alcohol, but is precipitated from these solutions by the least trace of an inorganic salt or base. It loses water of crystallisation at 100°, becoming rather darker in colour. Concentrated sulphuric acid dissolves it with a violet coloration, which changes to orange on dilution. The free acid is crystalline. It yields nitro and more highly sulphonated derivatives. When subjected to dry distillation diphenylenenaphthaquinoxaline is found. The constitution of the new sulpho-acid must be—



and its formation proves the correctness of Cléve's formula for naphthionic acid, and determines the position of the side-chains in congo-red. L. T. T.

β-Naphthylaminesulphonic Acid. By S. Forsling (*Ber.*, **19**, 1715—1716).—*β-Naphythylaminesulphonic acid*, $NH_2 \cdot C_{10}H_6 \cdot SO_3H$, is prepared by heating β-naphthylamine with strong sulphuric acid for some time at 140°. It forms slender white needles. The *potassium salt* forms microscopic needles very readily soluble in water. The *sodium* (with 4 mols. H_2O) and *barium salt* (with 4 to 6 mols. H_2O) were also prepared. The *diazo-compound*, $C_{10}H_6N_2SO_3$, forms a crystalline powder. When the diazo-compound is boiled with strong hydrochloric acid, the product treated with water and neutralised with potassium carbonate, and the salt so obtained heated with an equal weight of phosphorus pentachloride, a sulphochloride is obtained which melts at 128—129°; it is identical with that prepared by Arnell from β-chloronaphthalenesulphonic acid (comp. this vol., p. 555). N. H. M.

Synthesis of an Inactive Terpilenol. By G. Bouchardat and J. Lafont (*Compt. rend.*, **102**, 1555—1557).—When caoutchene (b. p., 175—178°), an inactive terpilene obtained by the dry distillation of caoutchouc, is heated with glacial acetic acid, the action is limited even at 150°, beyond which temperature the hydrocarbon polymerises rapidly. The product, terpilene acetate, $C_{10}H_{16},C_2H_4O_2$, is separated by distillation in a vacuum. It is a neutral liquid with an amber tint and aromatic odour, has no action on polarised light, becomes very viscous at — 50° but does not solidify, and boils at 110—115° in a vacuum, or at 220° under ordinary pressure with partial decomposition into acetic acid and the hydrocarbon; sp. gr. at 0° = 0·9705; vapour-density 6·6. When treated with hydrogen chloride, it yields a dihydrochloride identical with that from terpilene, and when heated with alcoholic potash at 100° it yields inactive terpilenol, $C_{10}H_{16}H_2O$. This terpilenol is a colourless viscous liquid, which boils at 114—118° in a vacuum; vapour-density 5·8. With hydrogen chloride, it yields the dihydrochloride first described, and it reacts violently with nitric acid. It crystallises with great difficulty, even at very low temperatures, owing to its tendency to remain in superfusion. The crystals are bulky and melt at 250°.

Only one acetate is formed under the conditions described, and in this respect caoutchene resembles inactive camphene but differs from terebenthene. This is further evidence that when the terebenthenes have once been converted into the more stable camphenes or terpilenes, these compounds retain their individualty and form two perfectly distinct isomeric series. C. H. B.

Isomerism of Camphols and Camphors. By A. Haller (*Compt. rend.*, **103**, 64—66).—The author has examined (1) a camphol which is known to the Chinese as camphor of N'gai, and is derived from *Blumea balsamifera*, D.C.; (2) a camphol known as Bang Phiên, which is derived from the same tree and is imported from Hanoï; (3) Martico camphor. Not only the camphols, but also the corresponding camphors, their monobromo-derivatives and the camphoric acids, were examined. The camphors were obtained from the camphols by the action of nitric acid, the bromo-derivatives by the direct

action of bromine, and the camphoric acids by heating for several hours with a large excess of nitric acid of sp. gr. 1·27. The camphols and bromine-derivatives were dissolved in toluene; the camphors and camphoric acids in alcohol. The following results were obtained:—

	1.		2.	
	M.p.	Rotatory power $[\alpha]_D$.	M.p.	Rotatory power $[\alpha]_D$.
Camphol.....	209°	— 37·77	208·9°	— 38·203
Camphor.....	177·5	— 42·10	178·6	— 42·76
Monobromocamphor	75·1	—127·60	76·1	—127·70
Camphoric acid....	185·0	— 38·83	186·2	— 46·33

	3.	
	M.p.	Rotatory power $[\alpha]_D$.
Camphol.....	—	—
Camphor.....	175·0	— 41·66
Monobromocamphor	75·1	—127·74
Camphoric acid	186·1	— 46·33

These results indicate that the three products are identical; the difference between the rotatory powers of the camphor of N'gai and Bang Phiên is doubtless due to the presence in the former of a small quantity of an inactive or lævogyrate camphol. C. H. B.

Cyano-camphor. By A. Haller (*Compt. rend.*, **102**, 1477—1479). —5 grams of cyano-camphor were dissolved in 100 c.c. of alcohol, saturated with hydrogen chloride, and the solution was allowed to stand at the ordinary temperature for a long time. After some months, ammonium chloride was precipitated, and at the end of three years the liquid was evaporated in a vacuum over potash and sulphuric acid, the residue washed with a solution of sodium carbonate, and dissolved in ether. The ethereal solution was dried over calcium chloride, the ether evaporated, and the oily liquid distilled. The greater part of the product consists of ethyl camphocarbonate,

$$C_{10}H_{15}O{\cdot}COOEt.$$

This compound is slowly saponified by alcoholic potash at the ordinary temperature, and the acidified liquid when extracted with ether yields camphocarbonic acid, which forms prismatic crystals, melting at 128—129°. It is evident from these reactions that cyano-camphor may be regarded as the nitrile of campho-carbonic acid.

Sodium camphocyanate, $C_{10}H_{14}NaCNO$, is obtained in slender needles by cooling a concentrated solution of cyano-camphor in an aqueous solution of sodium hydroxide. The crystals are stable when dry, but if exposed to the air they absorb moisture and carbonic anhydride. When freshly prepared they are soluble in alcohol, but they are decomposed by water with liberation of cyano-camphor.

Potassium camphocyanate, $C_{10}H_{14}KCNO$, is obtained in a similar manner. It forms nacreous unctuous plates with properties similar to those of the sodium-derivative.

It would seem that the metal in these compounds is in the same state as in the sodium and potassium derivatives of ethyl malonate, ethyl acetoacetate, ethyl benzoylacetate, &c. C. H. B.

Menthol-derivatives. By G. Arth (*Ann. Chim. Phys.* [6], **7**, 433—499).—Finely powdered menthol may be oxidised by treating it with an aqueous solution of potassium permanganate (containing 1·6 per cent. of the salt) acidulated with sulphuric acid, and exposing the mixture to sunlight at about 30° for some days, with occasional agitation. The purified oxidation product forms a colourless acid syrup, weighing about one-eighth of the menthol employed. On distilling this under 15 mm. pressure, a small amount of distillate is obtained between 120° and 130°, consisting of formic, propionic, and butyric acids; the greater part of the oxidation products, however, distils between 175° and 200°, and consists of *oxymenthylic acid*, $C_{10}H_{18}O_3$. This is a viscous liquid, boiling without decomposition at 173—175° under 15 mm. pressure. It is very sparingly soluble in water, but dissolves readily in alcohol and ether. *Silver oxymenthylate*, $C_{10}H_{17}AgO_3$, is soluble in boiling water, and crystallises in brilliant nacreous plates. The salts of the alkalis are very deliquescent colourless compounds. The magnesium, barium, and calcium salts are all very soluble in water, and do not crystallise well. A solution of sodium oxymenthylate forms a white precipitate with lead, brown with iron, greenish-blue with copper, and yellow with platinum salts.

Methyl oxymenthylate, $C_{10}H_{17}MeO_3$, forms a colourless liquid lighter than water, having a pleasant ethereal odour, and boils with partial decomposition at 136—137° under 17 mm. pressure. The corresponding ethyl salt is a similar compound boiling with partial decomposition at 145° under 15 mm. pressure. Oxymenthylic acid apparently has no alcoholic function, as on heating the ethyl salt with acetic chloride no aceto-compound is formed, neither does sodium amalgam exert any reducing action on it.

The fraction of the oxidation-products of menthol boiling above 200° forms about one-third of the whole; it has no constant melting point, is solid, of a waxy consistency, and distils between 200° and 212°. By treating it with ammonia, a crystalline salt is formed; this may be purified by washing it with dry alcohol. It yields the free acid when treated with sulphuric acid. It melts at 86 to 87·5°, is very soluble in water, and crystallises in a mass of slender needles. It dissolves readily in alcohol and in ether, and has the composition $C_7H_{12}O_4$. It is bibasic and isomeric with diethylmalonic, isobutylmalonic, and the pimelic acids, but has a much lower melting point than any of these. The author therefore proposes to call it β-pimelic acid, as it is closely allied to pimelic acid in its mode of formation. The silver salt, $C_7H_{10}Ag_2O_4$, is a white powder insoluble in boiling water.

By treating the sodium-derivative of menthol with cyanogen or cyanogen gas, *menthol-urethane*, $C_{10}H_{19}O{\cdot}CONH_2$, is obtained; by heating it with hydrochloric acid in a sealed tube, carbonic acid, ammonia, and water are formed. On digesting the urethane with acetic anhydride at 100°, no action takes place, but on raising the temperature to 130—135° carbonic anhydride is given off, and menthyl acetate and a

small amount of acetamide are formed. By dissolving the urethane in three times its weight of benzaldehyde and heating with 10 to 15 parts of concentrated hydrochloric acid, shaking frequently until the upper layer of benzaldehyde turns red, and then cooling the mixture, the upper layer of liquid solidifies to a crystalline mass of *benzylidene-menthyl urethane*, $C_{10}H_{19}\cdot CONH)_2CHPh$, which is separated, washed, and recrystallised from boiling alcohol, when it forms slender silky needles, and melts at 143°. It is decomposed by boiling it with water, and on heating it with dilute hydrochloric acid, benzaldehyde and menthol-urethane are again formed. On heating menthol-urethane above 200° it is decomposed, cyanuric acid being formed, and on heating the urethane in a reflux apparatus for several hours with the theoretical quantity of alcoholic potash, menthol, water, and potassium cyanide are formed.

Menthyl carbonate, $(C_{10}H_{19})_2CO_3$, may be obtained by boiling the mother-liquors from which the urethane was crystallised with excess of water, and cooling. It forms pearly crystals or large plates in the oblique system, melts at 105°, is sparingly soluble in alcohol, readily in benzene, toluene, and ether. Its solution in benzene is lævorotatory, $[\alpha]_D = -92{\cdot}52°$. On heating at 100° with the theoretical amount of alcoholic potash, it is completely saponified, but it is not acted on by alcoholic ammonia at 140°, and is only saponified on raising the temperature to 175°.

The so-called menthyl chloride of Oppenheim (*Bull. Soc. Chim.*, **100**, 1861) is in fact a hydrochloride of menthene, as on digesting it with silver acetate, menthene, acetic acid, and silver chloride are formed, but no menthyl acetate.

Menthyl benzoate, $C_{10}H_{19}\cdot BzO$, is prepared by heating the theoretical amounts of benzoic acid and menthol at 170° in sealed tubes for 48 hours. It crystallises well, melts at 54°, boils at about 230° with partial decomposition, is saponified by alcoholic potash, and when heated for 24 hours in a sealed tube at 250° is completely decomposed into benzoic acid and menthene. It crystallises in the rhombic system, and its solution in benzene is lævorotatory, $[\alpha]_D = -90{\cdot}92°$.

Normal menthyl succinate, $C_2H_4(COOC_{10}H_{19})_2$, is obtained by heating menthol and succinic acid in theoretical quantity at 150° in a sealed tube for 48 hours. It melts at 62° and boils with partial decomposition at 220°; on heating at this temperature in a sealed tube for several hours, it is completely decomposed into succinic acid and menthene. Its solution in benzene is lævorotatory, $[\alpha]_D = -81{\cdot}52°$. It crystallises in the rhombic system.

Hydrogen menthyl succinate, $COOH\cdot C_2H_4\cdot COOC_{10}H_{19}$, is obtained by heating succinic acid and menthol in molecular proportion for 40 hours at 110°. It melts at 62°, is very soluble in alcohol or ether, and but sparingly in water. Its solution in benzene is lævorotatory, $[\alpha]_D = -59{\cdot}63°$. It has acid properties, and compound normal salts, containing the alkaline and alkaline earthy metals, as also silver and gold, were prepared.

Normal menthyl orthophthalate, $C_{28}H_{42}O_4$, is obtained by heating the theoretical amounts of menthol and phthalic anhydride in sealed tubes for 40 hours at 135—140°. Its solution in benzene is lævo-

rotatory, $[\alpha]_D = -94{\cdot}72°$. It melts at 133°, and crystallises in the rhombic system.

Hydrogen menthyl orthophthalate, $C_{18}H_{24}O_4$, is obtained by heating the theoretical amounts of orthophthalic anhydride and menthol in a sealed tube at 110° for 36 hours. It forms a light white powder consisting of minute needles, is insoluble in water, hot or cold, but dissolves readily in alcohol, ether, or chloroform. It melts at 110°. Its solution in benzene is lævorotatory $[\alpha]_D = -105{\cdot}55°$.

The author finds that the specific rotatory power, $[\alpha]_D = -49{\cdot}40$ at 22°, of the menthol which he employed in his research, and which was most carefully purified, differs from that given by other authors. The menthene obtained by heating this menthol with phosphoric anhydride was dextrorotatory, its activity slowly increasing with each fresh distillation over the dehydrating agent. This is probably due to the slow removal of small quantities of unaltered lævorotatory menthol.

A. P.

Fisetin, the 'Colouring Matter of Fustet Wood, or "Young Fustic." By J. Schmid (*Ber.*, **19**, 1734—1749).—The author has investigated this subject anew. He finds that fisetin occurs in fustet (the wood of *Rhus cotinus*, L.) in the form of a glucoside which is combined with a tannin (probably sumach tannin). This compound is very easily broken up into the glucoside (to which the author gives the name *fustin*) and tannin by either alkalis or acids, and the supposed red and brown colouring matters of former investigators were probably only the coloured oxidation-products of this tannin. The *fustin-tannide* (the compound of the glucoside with tannin) was extracted with water, impurities precipitated by lead acetate in acetic solution, and the tannide extracted from the aqueous solution with ethyl acetate. Thus obtained it formed long yellowish-white needles, easily soluble in water, alcohol, and ether. The aqueous solution gives with ammonia a brown, with potash a brownish-red coloration. It reduces Fehling's solution. The substance is decomposed when heated above 200°. When dissolved in a little warm glacial acetic acid, and the solution diluted with water, the tannide yields yellowish-white lustrous needles of the glucoside *fustin*, $(C_{23}H_{12}O_5 : C_6H_{11}O_6)_2$. This substance begins to blacken at 200°, and melts with decomposition at 218—219°. It is easily soluble in boiling water, in alcohol, and in alkalis, sparingly in ether. With lead acetate or stannous chloride, it gives a yellow, with copper acetate a brown precipitate, all of which are soluble in acetic acid. Ferric chloride gives a green coloration, which, on the addition of dilute soda, changes through violet-blue to red. When warmed with dilute sulphuric acid, this glucoside is gradually decomposed into a sugar and fisetin, $C_{23}H_{10}O_3(OH)_6$. The fisetin thus obtained was identical with that obtained from cotinin, a commercial extract of fustet, prepared by extracting the wood with dilute soda. The author used cotinin as the source of the fisetin employed in his further experiments. Pure fisetin crystallises from dilute alcohol in small lemon-yellow prisms; from acetic acid in yellow prisms containing 6 mols. H_2O. It is sparingly soluble in ether, benzene, light petroleum, chloroform, and

boiling water, easily in methyl and ethyl alcohols and in ethyl acetate. The crystals lose their water at 110°, begin to blacken at 270°, but do not melt below 360°. It may be sublimed with partial decomposition to small needles. It gives characteristic precipitations and colorations with many metallic salts. Nitric acid oxidises it to oxalic and picric acids; 10 per cent. fuming sulphuric acid dissolves it, with formation of a sulphonic acid. It reduces Fehling's and copper solutions. Alkalis and carbonated alkalis cause an alcoholic solution to turn brownish-red, and produce fluorescence. The absorption spectrum is not very characteristic. It is very similar in properties to quercetin, from which it differs in composition by CO_2.

With acetic anhydride and sodium acetate, fisetin yields *hexacetofisetin*, $C_{23}H_{10}O_9Ac_6$, which crystallises in white needles sparingly soluble in boiling alcohol, benzene, and ethyl acetate, easily in chloroform; it melts at 200—201°. *Hexabenzoyl-fisetin*, $C_{23}H_{10}O_9Bz_6$ (prepared with benzoic anhydride) forms small white needles melting at 184—185°. It is sparingly soluble in alcohol, easily in chloroform. When heated with excess of benzoic chloride, fisetin forms a compound melting at 194—195°, and closely resembling the hexabenzoyl-derivative; it is probably a less highly benzoylated product.

Fisetin hexethyl oxide, $C_{23}H_{10}O_9Et_6$, is formed by the action of ethyl iodide and potash on fisetin. It forms long pale yellow needles melting at 106—107°, and easily soluble in alcohol, ether, benzene, &c. Its solutions no longer show the reactions characteristic for fisetin. *Fisetin hexamethyl oxide* formed pale-yellow needles melting at 152—153°. When fisetin is dissolved in a warm saturated solution of sodium carbonate, a *sodium-derivative*, $C_{23}H_{14}O_9Na_2$, crystallises out in yellow glistening needles. This compound is very unstable, and turns greenish-black on exposure to the air. A similar potassium-derivative was prepared. None of the metallic lakes were obtained of sufficiently constant composition to determine their composition. No hydroxylamine-derivative of fisetin could be prepared, neither could any ethyl salt be formed by the action of alcohol and hydrochloric acid, results which would point to the absence of carbonyl or carboxyl groups from the fisetin molecule. When fused with potash, fisetin yields phloroglucol and protocatechuic acid, the latter predominating. Sodium amalgam in alkaline solution causes the same decomposition, but in acid solutions a new reduction-product is obtained, which the author has not yet obtained in a pure state. L. T. T.

Acorin and its Derivatives. By H. Thoms (*Arch. Pharm.* [3], **24**, 465—481).—The bitter principle of the rhizome of *Acorus calamus*, L., was first investigated by Faust (*Arch. Pharm.*, 1867, 132, 214), who obtained a soft resin-like bitter principle of the colour of refined honey, to which he gave the name of *acorin*, and concluded from its reactions that it was a nitrogenous glucoside.

Hopff has shown that both vegetable and animal charcoal have the property of extracting the bitter principles from numerous bitter plants. The author employed freshly ignited bone charcoal to extract the principle from the aqueous solution. After two days' digestion of the charcoal, with frequent shaking, the bitterness of the liquid

had disappeared. The charcoal was collected on a filter, well washed, dried, extracted with 90 per cent. alcohol, and the filtrate distilled until a turbid aqueous solution remained. The last fraction of ethereal oils can be removed on the water-bath. On treating with ether and evaporating, a honey-yellow balsam is obtained with a faint aromatic odour and a strong, bitter, aromatic taste. The process yielded about 0·18 per cent. of acorin. The product thus obtained was found to be free from nitrogen, the nitrogen in Faust's product being due to the presence of impurity.

Acorin is insoluble in water, dilute acids, and alkalis, easily soluble in absolute alcohol, methyl alcohol, ether, benzene, toluene, chloroform, carbon bisulphide, and acetone. By long heating with dilute acids or alkalis, an odour of ethereal oil becomes clearly perceptible. Fehling's solution gives a faint sugar reaction. Attempts to obtain acorin in a crystalline form were unsuccessful. Heated to 85°, the colour darkens perceptibly. A considerable quantity was heated for several hours at 80°, and with this the subsequent investigation was conducted.

Analysis gave the formula $C_6H_{10}O$. The molecular formula of acorin was deduced from the amount of sugar obtained by the action of dilute acids and alkalis respectively. Discordant results were obtained, owing to the oxidising effect of the atmosphere, but the results became concordant when the reaction was conducted in hydrogen. The reaction is represented by the equation $6C_6H_{10}O = 3C_{10}H_{16} + C_6H_{12}O_6$; hence the molecular formula of acorin is $C_{36}H_{60}O_6$. Decomposition under the action of emulsin gave concordant results, whilst yeast and saliva failed to cause the formation of sugar, and superheated steam did not complete the decomposition. The ethereal oil formed during the above decomposition was produced in quantity by the action of aqueous soda in a current of hydrogen. After fractionating, the oil boiled at 158—159°, and had the composition $C_{10}H_{16}$. It has an odour of turpentine, is colourless, soluble in alcohol and ether, and has a sp. gr. of 0·8793 at 0°. A portion boiling at 250—255° had a bluish colour, which disappeared on boiling with metallic sodium, still the hydrocarbon, which now boiled at 255—288°, had the same composition, $C_{10}H_{16}$. It was sparingly soluble in alcohol, readily in ether.

Acoretin, $C_{36}H_{58}O_7$, the resin resulting from the action of dilute acids or alkalis on acorin, is a dark brown, gritty, bitter, viscid body, with a faintly aromatic odour and neutral reaction. It is easily soluble in alcohol, ether, chloroform, and acetone, insoluble in benzene. From its solvents, it separates in an amorphous state on evaporation. An attempt to induce further oxidation by heating with strong hydrochloric acid was unsuccessful. Acoretin was not reduced to acorin by the action of zinc and hydrochloric acid, but metallic sodium in the presence of water induced the reduction, as shown by the change in colour and odour of calamus. The resin extracted directly from calamus rhizome, when purified, was found to have the same composition as acoretin.

The author discovered in the calamus rhizome a crystalline alkaloïd, *calamine*, of strongly basic nature; it contains nitrogen. J. T.

Action of Alloxan on Pyrrolene. By G. Ciamician and P. Silber (*Ber.*, **19**, 1708—1714; compare this vol., p. 367).—Pyrrylalloxan, $C_8H_7N_3O_4$, is obtained by adding some drops of pyrroline to a not too dilute aqueous solution of alloxan; it separates in lustrous plates. If only a trace of an acid is present, a dye is formed, and it is very difficult to get the substance quite colourless. It is insoluble in ether, benzene, and light petroleum, soluble in water; when heated it does not melt. Prolonged boiling with water decomposes it. The *silver compound*, $C_8H_5N_3O_4Ag_2$, was prepared; it detonates when heated and decomposes on exposure to light.

Methylpyrrylalloxan, $C_8H_6N_3O_4Me$, is prepared from methylpyrroline in a manner similar to the above compound. It is readily soluble in hot water, sparingly in alcohol.

When pyrrylalloxan is added to a 50 per cent. solution of caustic potash, the whole becomes warm and gives off ammonia; if acetic acid is then added, crystals of a compound, $C_7H_6N_2O_3$, separate, and carbonic anhydride is given off. The new substance crystallises from ethyl acetate in white plates, readily soluble in warm alcohol and water, less soluble in ether. When boiled for a long time with water, the solution becomes red, and an amorphous scarlet mass is obtained, which afterwards becomes brown. The *silver* compound, $C_7H_5AgN_2O_3$, forms a white precipitate; this, when treated with methyl iodide, yields a *methyl-derivative*, $C_7H_5MeN_2O_3$. The latter crystallises from hot ethyl acetate in white plates, soluble in water and alcohol, insoluble in ether and light petroleum. It decomposes and melts at 160—170°.

The following constitutional formulæ are suggested for pyrrolalloxan and for the compound obtained from it by the action of potash: $C_4NH_4{\cdot}CO{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}CONH_2$ and $C_4NH_4{\cdot}CO{\cdot}CO{\cdot}CONH_2$.

N. H. M.

Alkaloïds. By O. de Coninck (*Compt. rend.*, **102**, 1479—1481; and **103**, 62—63).—Pyridine methiodide, C_5H_5NMeI, when heated with alcoholic potash at 45°, yields a brown resin, which dissolves in alcohol with formation of a deep red solution. This solution is turned bright-red by hydrochloric acid, orange-red by acetic acid, and ruby-red by ammonia, or dull-red if the ammonia is added in excess. The tints vary with the strength of the original alcoholic solution; if it is very concentrated, hydrochloric acid produces a dark brown resinous precipitate.

Pyridine ethiodide, C_5H_5NEtI, under the same conditions, yields a colouring matter, which with alcohol forms a carmine-red solution giving the reactions just described. The methiodide and ethiodide of α-picoline behave in a similar manner. The colouring matters obtained from the pyridine-compounds are not fluorescent, but in presence of acids they possess considerable tinctorial power.

The formation of these substances may be used as a test for a pyridic base. 1 c.c. of the isolated base is gradually mixed with 2 c.c. of methyl iodide, the liquid being cooled during the mixing. Energetic combination takes place, and the crystalline product is dissolved in 5—6 c.c. of alcohol, heated to boiling, and potash solution

of 45° is dropped in. A blood-red colour is produced and the liquid finally becomes dark brown. Reactions of the same kind are obtained when the pyridic compounds are mixed with corresponding derivatives of the quinoline bases.

Pyridine methiodide, when mixed with quinoline methiodide, yields a brown resin, soluble in alcohol, with formation of a dark-red solution, which is turned pale brown by acids and dull red by alkalis. A large excess of alkali tends to decolorise the solution, especially if it is diluted with water. In a concentrated solution, hydrochloric acid produces an abundant precipitate. With mixtures of quinoline methiodide with pyridine ethiodide, and of quinoline ethiodide with pyridine methiodide, the colours obtained vary with the nature of the alcoholic radicle and the position which it occupies.

Similar reactions are obtained with the dipyridines. An alcoholic solution of α-dipicoline methiodide becomes greenish-blue in presence of potash, but hydrochloric acid discharges the colour. β-Dipicoline methiodide gives a similar reaction. β-Dilutidine methiodide becomes greenish-brown in presence of potash. On addition of hydrochloric acid, a brown precipitate is formed, and the liquid is left practically colourless. γ-Dilutidine methiodide gives an almost identical reaction. C. H. B.

Colour Reactions for Determining the Constitution of Carboxylic Acids of the Pyridine, Quinoline, and Allied Series. By Z. H. Skraup (*Monatsh. Chem.*, **7**, 210—215).—In aqueous solution, many of the carboxylic acids of the above series give a coloration, with ferrous sulphate, varying from yellow to brownish-red, whilst others give no coloration. The author has examined a very large number of these acids of known and unknown constitution, and finds that the red coloration is only given by acids which have a carboxyl-group in the α-position. This rule does not appear to be affected by the introduction of side-chains.

When the carboxyl-group is situated in the benzene-ring, the red coloration is not given by the acids in aqueous solution.

G. H. M.

Action of Ethyl Acetoacetate and Ethyl Acetonedicarboxylate on Hydrazobenzene. By H. v. Perger (*Monatsh. Chem.* **7**, 191 — 197). — Phenylmethyloxyquinizine, $C_9NH_6(:NPh)MeO$ [$=1',2':2':4$], is obtained by heating a mixture of hydrazobenzene (1 mol.) and ethylic acetoacetate (1·5—2 mols.) at 120° for 4 to 5 hours, and then allowing it to cool. It may be purified by successive crystallisations from hot dilute hydrochloric and sulphuric acids and hot water. Thus obtained, it forms white needles, melts at 122°, is only slightly soluble in cold water, but readily in alcohol, ethyl acetate, and glacial acetic acid. It is a feeble base, giving a crystalline hydrochloride and a crystalline platinochloride, $(C_{16}H_{14}N_2O)_2,H_2PtCl_6$. It gives none of the reactions for benzidine or diphenyline.

Hydrazobenzene (1 mol.) heated at 120° for 4 to 5 hours with ethylic acetonedicarboxylate (2 mols.) gives a mass which, after saponification with sodium hydrate and subsequent purification, yields

crystals agreeing in all respects with the above phenylmethyloxyquinizine.

The author considers that these results confirm the view that hydrazobenzene is a symmetrical secondary hydrazine.

G. H. M.

Action of Ethyl Acetoacetate on Hydrazobenzene. By A. Müller (*Ber.*, **19**, 1771—1772).—When heated in closed tubes at 100—150°, hydrazobenzene and ethyl acetoacetate react on one another, alcohol and a compound, $C_{16}H_{14}N_2O$, being formed. The latter forms crystals which contain $\frac{1}{2}$ mol. H_2O, melts at 120°, and is easily soluble in alcohol and ether, sparingly so in water. It has the properties of a feeble base and a feeble acid. It dissolves more readily in dilute acids and alkalis than in water, but these solutions on cooling deposit the base unchanged. Its *platinochloride* crystallises in golden-yellow scales. This base is probably a phenylated quinizine, $C_9NH_6(:NPh)MeO$ [= 1′, 2′ : 2′ : 4′]. L. T. T.

Caffeine. By E. Schmidt (*Arch. Pharm.* [3], **24**, 522—528; compare Abstr., 1883, 872—873; 1884, 338).—Caffeine methhydroxide is obtained by the action of moist silver oxide on caffeine methiodide. It forms colourless, feathery needles, easily soluble in water, alcohol, and chloroform, but almost insoluble in ether and light petroleum. Its composition is $C_8H_{16}N_4O_2,MeOH + H_2O$. It melts at 90—91°, or when freed from water, at 137—138°. From this investigation it appears that caffeine methhydroxide differs from the analogous quaternary ammonium bases in yielding not methylcaffeine, but caffeine on dry distillation. The presence of methylamine and cholestrophane in the distillation-products is most probably due to secondary reactions. J. T.

Reactions of Morphine. By J. Donath (*J. pr. Chem.*, [2], **33**, 563—564).—When an intimate mixture of morphine, potassium arsenate, and sulphuric acid is heated, a blue-violet coloration is produced, turning a dark brown-red on further warming. On moderate dilution with water, a red colour is formed, but if chloroform is added it gives a violet dye. Dehydromorphine under the same conditions gives a green coloration, but no dye with chloroform. Morphine heated with potassium chlorate and concentrated sulphuric acid gives a grass-green coloration. V. H. V.

Dehydromorphine (Oxydimorphine). By J. Donath (*J. pr. Chem.*, [2], **33**, 559—562).—According to the author, the substance named pseudomorphine or oxydimorphine is best designated by the term dehydromorphine, as derived from morphine by the removal of two atoms of hydrogen. A good test for this compound consists in heating it with sulphuric acid (2 parts of acid to 1 of water) until the vapours of sulphuric anhydride are evolved; the liquid is of a blue-green colour, turning a rose-red on moderate dilution, and a deep violet on addition of an oxidising agent. It resembles morphine in its reactions with ferric chloride, concentrated nitric acid, Frohde's

reagent and iodic acid; but it is more sparingly soluble in most solvents than morphine. Its hydrochloride gives precipitates with most of the ordinary alkaloïd reagents. The specific rotatory power of the hydrochloride for $p = 0{\cdot}951$, $t = 24°$, is $[\alpha]_D = -103'\ 13°$.

Dehydromorphine is not reduced to morphine by sodium amalgam or by hydrochloric acid with zinc or tin. V. H. V.

Oxydimorphine. By K. Polstorff (*Ber.*, **19**, 1760—1762).—The author upholds the formula $C_{34}N_2H_{36}O_6$ previously proposed for this substance by himself and Broockmann. Since both the author and Donath have obtained 70 and 80 per cent. of oxydimorphine by the oxidation of morphine with equal molecular proportions of potassium ferricyanide, the reaction must take place according to the equation $C_{17}H_{19}NO_3 + KOH + K_3FeCy_6 = C_{17}H_{18}NO_3 + K_4FeCy_6 + H_2O$, as a larger proportion of ferricyanide would be required for the formation of a compound, $C_{17}H_{17}NO_3$. L. T. T.

Alcoholates of Conchinine. By F. Mylius (*Ber.*, **19**, 1773—1776).—Hesse states (Abstr., 1878, 434) that conchinine crystallises from alcohol with $2\frac{1}{2}$ mols. H_2O. The author finds, however, that this is not the case, but that the crystals contain 1 mol. of alcohol which they lose at 120°. Conchinine is also capable of forming similar crystalline compounds of the general formula $C_{20}H_{24}N_2O_2 + R{\cdot}OH$ with other alcohols. The methyl, propyl, and allyl alcohol-derivatives have been prepared and examined. A similar compound crystallising in plates is formed with glycol, but it contains 2 mols. conchinine to 1 of glycol. L. T. T.

Decomposition of Pilocarpine. By E. Hardy and G. Calmels (*Compt. rend.*, **102**, 1562—1564).—When pilocarpine is boiled rapidly and continuously with a large quantity of water for about 12 hours, it splits up into equal molecules of trimethylamine and β-pyridine-α-lactic acid.

β-Pyridine-α-lactic acid, $C_8H_9NO_3$, is a gummy, non-crystallisable substance, very soluble in water and alcohol. The hydrochloride, platinochloride, and aurochloride have also the same properties, and all lose hydrochloric acid very readily. The platinochloride changes to prismatic needles of the composition $(C_8H_9NO_3)_2PtCl_4$, and the aurochloride changes to silky, striated, yellow prismatic needles of the compound $C_8H_9NO_3,AuCl_3$, which melt at 153—154°. Both modified compounds are soluble in alcohol. β-Pyridine-α-lactic acid forms gummy compounds with alkalis, which are insoluble in alcohol of 80°, and are not decomposed by carbonic acid. The barium salt is a white hygroscopic powder insoluble in alcohol and ether. Solutions of the acid give no precipitate with copper salts and no precipitate with silver nitrate unless the solution is concentrated.

Fuming nitric acid has no action on pilocarpine, a result which is doubtless connected with the fact that this acid has no action on pyridine or trimethylamine.

Pilocarpine is oxidised by potassium permanganate with formation of methylamine, a small quantity of ammonia, and β-pyridinetartronic

acid, with traces of β-pyridine-carboxylic acid, which can be separated by means of cupric acetate.

β-Pyridinetartronic acid, $C_8H_7NO_5$, is a non-crystallisable syrup. If its hydrochloride is heated with alcohol, it loses hydrochloric acid, and forms a di-ethyl salt, a viscous oil which is insoluble in water and dilute alkalis, but is decomposed by hot alkalis. The aurochloride does not crystallise. β-Pyridinetartronic acid is bibasic, and with alkalis forms salts which have an alkaline reaction, are insoluble in absolute alcohol, very slightly soluble in alcohol of 50°, and are not decomposed by carbonic anhydride. The barium salt is insoluble in alcohol and ether, but dissolves in water, and if the solution is evaporated it yields a gummy mass which gradually loses water and forms a confusedly crystalline mass of the hydrate $BaC_8H_5NO_5,3H_2O$. The silver salt is slightly soluble in water. Copper acetate produces a precipitate only after addition of alcohol, and the then acid liquid contains the acetate of the acid.

This acid is oxidised by moderately concentrated potassium permanganate, and yields only β-pyridinecarboxylic acid.

C. H. B.

Conessine. By K. Polstorff (*Ber.*, **19**, 1682—1685).—Conessine (this vol., p. 372) was found to be present in East Indian *Holarrhena* to the extent of 0·08 per cent. It was purified by dissolving it in very dilute acetic acid, almost neutralising with ammonia, treating with lead acetate, and removing the lead by means of hydrogen sulphide. After repeating this treatment four or five times an almost colourless solution is obtained. The *nitrate*, $C_{12}H_{20}N,HNO_3$, forms small needles; the picrate (with 1 mol. H_2O) crystallises from alcohol in broad, lustrous, gold-coloured needles, which explode violently when heated.

The author considers the substance to be identical with that obtained by Haines from *Wrightia* (*J. Pharm.* [2], **6**, 432). The results of analyses of Haines' compound made by Warnecke (this vol., p. 372) agree with the formula $C_{12}H_{20}N$, as well as with $C_{11}H_{18}N$. Also the reaction given by Warnecke for Haines' compound holds good with conessine from *Holarrhena*. N. H. M.

Physiological Chemistry.

Nutritive Value of Albumin and Flesh Peptone. By S. Pollitzer and N. Zuntz (*Bied. Centr.*, 1886, 371—373).—The experiments were made on a dog, fed with 70 grams of rice starch, 20 grams of suet, and either flesh-peptone, gelatin, or albumoses containing equal quantities of nitrogen. The results show that peptone and hemialbumoses have the same nutritive value as flesh, and the increase of nitrogen stands in strong opposition to the loss of nitrogen incurred by feeding with gelatin. Zuntz experimented with com-

mercial peptone prepared by the action of superheated water, as to its value compared with flesh. American peptone was found to be incapable of replacing flesh, as it does not replace the excreted nitrogen, but if rice starch is given at the same time, these peptones are more nourishing than they would otherwise be. E. W. P.

Presence of Diastatic and other Ferments in Urine. By E. Holovotschiner (*Chem. Centr.*, 1886, 327).—The author has established the presence of ptyalin and similar ferments in urine. The proportion reaches a maximum 4—6 hours after eating. Urine was also found to contain a ferment having the property of coagulating milk. C. F. C.

Composition of Suint. By A. Buisine (*Compt. rend.*, **103**, 66—68).—The composition of suint is extremely complicated, but it may be divided into two parts, one the product of the sudoric secretion, soluble in water; the other the product of the sebaceous secretion, insoluble in water. The aqueous solution contains free carbonic anhydride; ammonium carbonate (from urea); potassium carbonate; acetic, propionic, butyric, valeric, and caproic acids; the higher fatty acids, including œnanthylic and caproic acids; oleic, stearic, and cerotic acids, and other acids which are found in waxes; fats in the form of an emulsion; phenol in the form of potassium phenylsulphonate; sarcolactic acid; benzoic acid (from hippuric acid); oxalic, succinic, and uric acids; the amido-acids glycocine, leucine, and tyrosine; and colouring matters similar to those of urine.

It is evident that the sudoric secretion contains those substances which are usually found in the urine of herbivorous animals, or the products of decomposition of such substances, together with a number of fatty acids. In the order of their abundance, the acids rank as follows: acetic, propionic, benzoic, lactic, capric, &c. The suint solution contains these compounds in such quantities that it might readily be used as a source for their extraction. The suint from an Australian fleece gave for 100 parts of dry residue 7·1 parts of acetic acid, 4 parts of propionic acid, 2·6 of benzoic acid, 2·5 of lactic acid, and 1 part of capric acid. C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

Formation of Starch in Leaves supplied with Sugars, Mannitol, and Glycerol. By A. Meyer (*Ann. Agronom.*, **12**, 209—220; from *Bot. Zeit.*, 1886, No. 5, and following).—The author's experiments were conducted in the following manner:—A starch-forming plant was chosen, and a whole branch of it surrounded with blackened paper; a leaf was removed from this branch daily, and tested for the disappearance of starch by Sach's method of successive immersion in boiling alcohol and solution of iodine. A day or two after the dis-

appearance of the starch the branch was cut off, and the several leaves cut in half, one set of halves being tested individually for starch. The portions of leaf free from starch were then cut into pieces of 4—6 square cm., which were floated, surface downwards, on a 10 per cent. solution of the sugars, &c., tried, experiment having shown this to be the most suitable strength. The solutions were contained in shallow glass dishes, loosely covered with glass plates, and were set aside in the dark at a temperature of 15°. At the end of some days, the leaves were removed from the solutions and tested again for the presence of starch. A great many plants were tried.

Dextrose, lævulose, and galactose are all transformable into starch in this way. A few plants can form starch from all three. Almost all the plants formed starch from lævulose, a few from dextrose, and very few from galactose. Trials with inosite yielded negative results. All the plants tried, except one, formed starch from saccharose, and the formation appears to be independent of the inversion of the sugar. Lactose yielded negative results only. Maltose gave rise to starch in the leaves of the beet, lilac, and dahlia. Raffinose, tried with beet leaves only, formed no starch. Mannitol was transformed into starch by the leaves of several plants of the *Oleaceæ*, in which mannitol occurs naturally, but not by leaves and plants which are usually free from mannitol. Dulcite in a saturated solution (3 per cent.) was tried with several plants which naturally contain it. Fusain leaves only showed the formation of starch after nine days. Erythrite gave negative results. Glycerol was transformed into starch by a large number of plants, amongst them being beet, dahlia, and *Cocalia suaveolens*. The author considers that the glycerol is first transformed into dextrose, thus :—$2C_3H_5(HO)_3 + O_2 - 2H_2O = C_6H_{12}O_6$.

J. M. H. M.

"Soluble Starch" and its Physiological Function in Vegetation. By J. Dufour (*Ann. Agronom.*, **12**, 297—298; from *Bull. Soc. Vaudoise des Sciences Naturelles*, **21**, No. 93).—The so-called "soluble starch" found in the cell contents of the epidermis of certain plants is considered by Kraus to be really a tannin. The author's observations tend to show that at any rate it is not a carbohydrate analogous to ordinary starch. It may be a glucoside, but it gives none of the reactions of tannin with ammonium molybdate, ferric chloride, potassium dichromate, and gelatin. The author does not concur in Nägeli's suggestion that it is an albuminoïd.

The plants containing most of this substance are *Saponaria officinalis* and *Gypsophila perfoliata*, *Arum Italicum*, *Bryonia dioïca*, several species of *Hordeum*, *Ornithogalum umbellatum*, and *Gagea lutea* also contain it. In all these plants, it occurs in the epidermis, but Nägeli believes that a similar body exists in various seeds (*Anagyris fœtida*, *Peganum harmala*, &c.). A fragment of the epidermis of *Saponaria officinalis* is speedily coloured an intense violet when immersed in iodised potassium iodide. An alcoholic tincture of iodine produces the same effect only after evaporation of the alcohol, when the blue compound is deposited in crystalline needles. The alcoholic extract of leaves of *S. officinalis*, treated with ether to dissolve out chlorophyll, &c., and then with water to dissolve out the "soluble starch,"

yields a yellowish neutral solution. A drop of this evaporated on a glass slide deposits yellowish spheroidal crystals, with radial lines but no trace of concentric striæ. These crystals do not swell out in hot water like starch granules. J. M. H. M.

Ratio of Starch to Sugar in Tobacco Leaves. By H. Müller (*Bied. Centr.*, 1886, 409—414).—The questions to be answered were as to whether fermentation, drying, and other processes of manufacture affect the percentage of starch in the leaves, also whether the ripe leaves store as much starch as the younger ones, and what influence this storing has on the weight and quality of the tobacco. A large number of fermented leaves from various sources were examined, and there appeared to be great irregularity in the quantity of starch present. As a rule, the best sorts contained more starch than the poorer, but not invariably so; three samples of finest Havana contained no starch at all. A law is enunciated that fermented tobacco contains as a rule little or no starch or no sugar, and the amount of starch present bears no relation to the quality of the tobacco. The ripeness and the method of drying the leaf have a great effect on the amount of starch present; rapidly dried leaves have most starch, as also those which have been injured, for thereby the moisture of the leaf evaporates, and the cells dry up before the conversion of starch can occur. The speckling of leaves occurs as they ripen, and is occasioned by starch accumulating in the chlorophyll grains until the chlorophyll is finally replaced. Absence of light greatly influences the quantity of starch in the leaf; one half of a leaf examined in the morning had lost four-fifths of its starch as compared with the other half examined the previous evening. The following table will be of interest:—

	Two green leaves.		Three ripening leaves.		Two ripe leaves.	
	6 P.M.	7 A.M.	6 P.M.	7 A.M.	6 P.M.	7 A.M.
Surface in sq. m.	463·5	442	996·6	1003	454	450
	gr.	gr.	gr.	gr.	gr.	gr.
Dry matter, gr.	2·20	1·96	5·63	5·42	2·97	2·72
Sugar in 100 gr. dry matter	1·25	0·60	1·05	0·63	0·81	0·41
„ 1 sq. m. surface	0·59	0·27	0·59	0·34	0·13	0·23
Starch in 100 gr.	31·79	26·74	38·42	33·30	42·62	76·95
„ 1 sq. m. surface	14·89	11·81	21·71	17·87	27·84	22·31

Besides the period of the day affecting the percentage of starch, it was found that the position of the leaf on the plant also influences it, the upper leaves being richest in starch.

The changes which occur during the drying of the leaves are as follows:—The whole of the starch disappears during the first days if the drying is not too rapid; the sugar thus formed is often con-

verted into water and carbonic anhydride, and this change seems to become complete in leaves quickly dried. The last trace of sugar disappears when fermentation sets in, whilst the residue of starch does not appear to be altered. E. W. P.

Biological Significance of Organic Acids. By WARBURG (*Ann. Agronom.*, **12**, 272—289; from *Untersuch. aus d. Botan. Instit. zu Tübingen*, **2**, 53—150).—The principles brought out in this critical discussion of the most recent researches of the author, de Vries, Krauz, Meyer, &c., are the following:—

The diminution of acidity during exposure to light is a property possessed not only by the fatty plants but by many others, such as *Pancratium*, *Saxifraga*, *Polygonum*, *Acacia*, *Rhododendron*, *Laurus*, *Ilex*, *Pinus*, *Ceratozamia*, *Polypodium*, &c., plants belonging to the most diverse families, but agreeing in the fact of being specially protected against rapid transpiration, as is roughly evidenced by the fact that their leaves wither very slowly when cut.

The organs containing no chlorophyll, and etiolated leaves suffer no diminution of acidity on exposure to light; this phenomenon occurs only in assimilating cells.

The most refrangible portion of the spectrum is least favourable to deacidification.

There is an evident relation between assimilation and deacidification, notwithstanding that deacidification will take place in an atmosphere deprived of carbonic anhydride; in this case it is possible that this gas is formed during deacidification, and immediately decomposed in the light.

Deacidification ceases entirely when leaves are killed by heat or by ether or chloroform; it is greatly encouraged by anything which favours access of oxygen, such as cutting the leaves into small pieces, and it may be almost prevented by plunging the plants into boiled water, or into an atmosphere of hydrogen, or by coating them with paraffin.

The author considers that both the formation and destruction of acids are phenomena of oxidation, or of respiration considered in its widest sense. The acids of fatty or oily plants are produced by incomplete oxidation, and they assist further oxidation in unequal degrees, oxalic acid, for example, being more permanent than the others. They may also escape oxidation by conversion into salts, and in the oily plants they tend to accumulate, because these plants are more or less protected from ingress of oxygen. The most important and the most readily oxidisable of the vegetable acids is malic acid, which has been found in more than 200 species, that is to say, in nearly every case in which it has been looked for. It cannot accumulate in thin leaves very accessible to air, but only in the more protected tissues. The quantity of acids formed depends on the general activity of metamorphosis of immediate principles, and this explains the small proportion found in roots, and the much larger quantities found in young internodes, &c.

The production of acids is proportional—(1) to the intensity of metamorphosis of immediate principles; (2) to the difficulty of access

of oxygen. The destruction of acids is proportional—(1) to the intensity of metamorphosis of immediate principles; (2) to the free access of oxygen; (3) to the temperature. J. M. H. M.

Occurrence of Vanillin in Assafœtida. By E. Schmidt (*Arch. Pharm.* [3], **24**, 534—535).—P. Lemcke and C. Denner, under the direction of the author, have succeeded in extracting a small quantity of vanillin from *assafœtida* by the following process:—The powdered resin was repeatedly extracted with ether, the filtrate shaken up with concentrated hydrogen sodium sulphite solution, and the liquid thus obtained supersaturated with dilute sulphuric acid. After expelling sulphurous anhydride the extraction with ether and subsequent treatment was repeated, and a third extraction made. After removing the ether by distillation, the resulting vanillin was dissolved in water, and the filtered solution allowed to evaporate over sulphuric acid. Well-formed crystals were thus obtained. J. T.

A Constituent of the Root of Pæonia Moutan. By W. Will (*Ber.*, **19**, 1776—1777).—The author has found peonal,

$$COMe\cdot C_6H_3(OMe)\cdot OH\ [COMe : OH : OMe = 1 : 2 : 4],$$

a substance lately investigated by Nagai, in the root of *Pæonia moutan*. L. T. T.

Growth of Wheat after Sugar-beet and after Potatoes. By E. Gatellier (*Bied. Centr.*, 1885, 403—404).—Wheat was grown on a plot one half of which had previously borne potatoes, the other half sugar-beet. Varying quantities of Chili saltpetre, as also of superphosphate, were added. Harvest showed that the beet had taken a great deal more out of the ground than the potatoes had, also that beet had taken more nitrogen than potatoes. E. W. P.

Composition, Nutritive Value, and Produce of the Permanent Grasses. By D. Wilson (*Trans. Highland and Agric. Soc. Scot.*, 1886, 148—187).—The author has made a new series of analyses of some of the permanent grasses upon the following plan. The seeds of the different grasses were verified as to purity by Carruthers, and were sown in long rows of the same size, 2 feet between each row, in a well cleaned old garden soil consisting of stiffish loam without manure. Each plot was divided into two equal parts, A and B.

Three cuttings of each portion were taken, each cutting being weighed separately.

June 3, 1885. First cutting, A.—The majority of the grasses coming into bloom.

July 13, 1885. First cutting, B.—Seed of grasses more or less ripe; clover in flower. Time of cutting the meadow hay of the district.

August 25, 1885. Second cutting, A.—Most of the grasses past bloom. Some seeds approaching ripeness.

September 25, 1885. Second cutting, B.—Earliest grasses beginning to show bloom; not so advanced as second cutting A.

October 12, 1885. Third cutting, A and B.—Undergrowth of young green shoots on A; very little on B. Full analyses were made of the first and third cuttings of A and the first cutting of B.

In the second cuttings of A and B the dry matter and albuminoïds, and in some cases the fibre and non-albuminoïd nitrogen, were determined. The first cutting of A represents hay cut at the right time, the first cutting of B overripe hay, and the third cutting of A young succulent shoots.

Mode of Analysis.—Samples of 200—300 grams were air-dried and weighed, then cut into small pieces and bottled for analysis. The moisture in the air-dried grasses was determined by heating to 110—112° in a current of dried air. "Fat, wax, and chlorophyll" were determined by exhausting with carbon bisulphide in a Soxhlet tube. The author considers that in the case of the first cutting A 35 per cent. of this extract is fat, in the case of the first cutting B 50 per cent., and of third cutting A only 25 per cent. Total nitrogen was determined by a soda lime combustion, and albuminoïd nitrogen by Stützer's copper hydroxide method. The "indigestible" albuminoïds were determined by a modification of Stützer's process of digestion with acid pepsin as follows:—2 grams hay in fine division were repeatedly triturated with cold water, and the liquid poured through a filter. The residue was finally transferred to the filter and washed until the washings were colourless. The residue on the filter was then transferred to a bottle by means of 100 c.c. water, containing 1 gram of 33 per cent. HCl, and 0·1 gram of good pepsin. The bottle was loosely stoppered and immersed in a water-bath kept at 40° for five hours, with occasional shaking. The solution was then filtered, the residue washed until free from acid, dried, and the nitrogen determined by a soda lime combustion. Nitrogen as nitrates and ammonia was not determined, as being too small. The ash was obtained by charring at a low red heat, extracting with water, igniting the insoluble portion in a muffle, and adding its weight to that of the water residue. The fibre was obtained by Henneberg and Stohmann's method; the ash contained was weighed and deducted, but not the nitrogen, which must be very small. In stating the results of analysis, the factor 6·25 was used both for albuminoïd and non-albuminoïd nitrogen, in order to facilitate comparison with older analyses. The extractive matter free of nitrogen was obtained by difference. The produce of hay on the different plots was calculated on a uniform basis of 14·3 per cent. of water.

An attempt to compare the nutritive values shown by the analyses has been made on the following lines. At the Continental agricultural stations, albuminoïds and fat are reckoned as respectively $4\frac{3}{4}$ and 4 times the value of carbohydrates. The author multiplies the digestible albuminoïds by 7, the indigestible albuminoïds by 4, and the "non-albuminoïd nitrogen × 6·25" by 2. In order that the real percentage of oil should be multiplied by 4, the author multiplies the "fat, wax, and chlorophyll" in first cutting A by $1\frac{1}{2}$, in first cutting B by 2, and in third cutting A by 1. For instance, the dry matter

in the first cutting of cocksfoot yields the number 100 when treated in this way—$(3{\cdot}21 \times 7) + (5{\cdot}73 \times 4) + (3{\cdot}25 \times 2) + (3{\cdot}36 \times 1\frac{1}{2}) + (43{\cdot}73 \times 1) = 100$—and the nutritive value of the other grasses is compared with this as a standard. The "value of produce" has been measured by multiplying the weight of dry matter by the figure denoting its nutritive value, and rejecting the last figure of the product in order to obtain a simpler expression.

The albuminoïd ratio of the tables is the ratio of *true* albuminoïds, taken as 1, to the sum obtained by adding the "extractive matter free from nitrogen" to $2\frac{1}{2}$ times the *true* fat. The numbers for the ratio of digestible albuminoïds to digestible carbohydrates and fat would be much greater, probably 1 : 11 or 12 instead of the average of 1 : 5·7. Almost all the grasses contain an excess of carbohydrates compared with digestible albuminoïds.

The tables given by the author are here condensed and rearranged with the exception of the partial analyses of the second cuttings A and B, and some lines of figures which can be obtained by simple calculation from those given. The percentage composition of the dry matter is also omitted for this reason.

From these tables it will be seen that the difference in composition between different cuttings of the same grass is far greater than that between different grasses cut at the same stage. Highest of all in nutritive value are the young slender shoots of the latest cutting on October 12. As the grasses advance to maturity the percentage of water diminishes greatly, the albuminoïds per cent. of dry matter diminish, and so do the ash and oil; the woody fibre and extractives free from nitrogen increase. The largest proportion of digestible albuminoïds is found when the grass contains most total albuminoïds.

Cocksfoot, although in nutritive value about 6 per cent. inferior to the average of the rest, surpasses them all in yield, and in the total value of the produce. Meadow foxtail gave the best value in the first cut, but suffers more than any of the rest from late cutting, and the aftermath of a late first cutting is small.

The first cut of meadow fescue surpassed all the other grasses in nutritive value, but it is not productive in autumn.

Sweet vernal was not deficient either in productiveness or nutritive value. Golden oat grass produced more than any other in the second and third cuttings, and is a good late grass; it is slightly inferior to cocksfoot in nutritive value. Perennial rye grass gains by a delay in the first cutting, whereas all the other grasses suffer loss. Portion B, cut late, yielded more than a third more produce than portion A. In nutritive value, it is equal or superior to cocksfoot. In produce and nutritive value combined, it is by no means so inferior as has been stated. If cocksfoot, foxtail, meadow fescue, and rye grass be each cut at their best, *i.e.*, the three natural grasses early, and the rye grass later, the total value of the rye grass will be inferior to that of the cocksfoot in the proportion of 5 to 7, and to that of the foxtail in the proportion of 5 to 6, and it will be nearly equal to that of meadow fescue. Fine leaved sheep's fescue yielded so little at the first cutting that the whole plot was cut; in all its stages it proved to be the richest of the grasses. Yarrow surpassed in nutritive value all the

I.—*Cutting of Portions A on June 3rd.*

Composition of the fresh herbage.	Cocksfoot.	Meadow fox-tail.	Tall fescue.	Meadow fescue.	Sweet vernal.	Golden oat grass.	Timothy.	Perennial rye grass.	Wood meadow grass.	Rough-stalked meadow grass.	Crested dogs-tail.	Hard fescue.	Average of 12 grasses.	Fine-leaved sheeps' fescue.	Perennial red clover.
Water	83·56	82·76	81·42	81·12	83·11	79·50	80·06	82·16	72·95	77·49	76·75	73·72	79·55	70·41	86·78
Digestible albuminoïds	0·53	0·74	0·83	0·92	0·90	0·74	0·75	0·70	1·10	0·87	0·89	1·19	0·85	2·02	2·09
Indigestible „	0·94	1·00	0·77	1·06	0·76	0·77	0·97	0·88	1·19	0·81	1·04	1·38	0·96	1·64	1·05
Non-albuminoïd N × 6·25	0·54	0·63	0·75	0·80	0·69	0·85	0·65	0·64	0·68	0·60	0·95	1·03	0·73	0·81	0·53
Fat, wax, and chlorophyll	0·55	0·47	0·58	0·63	0·29	0·46	0·48	0·69	0·62	0·75	0·70	0·67	0·58	1·21	0·68
Extractive matter free from nitrogen	7·19	7·22	7·82	8·72	8·03	9·32	9·64	8·22	12·26	11·86	11·28	11·50	9·42	12·66	5·31
Ash	1·48	1·66	1·92	1·43	1·44	1·99	1·68	1·65	2·26	2·04	2·16	1·85	1·80	2·29	1·46
Woody fibre	5·21	5·52	5·91	5·32	4·78	6·37	5·77	5·06	8·88	5·58	6 23	8·66	6·11	8·96	2·10
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Weight of green grass	994	900	786	582	784	576	610	636	385	437	182	173	—	82	89
Containing dry matter	163·4	155·2	146·1	109·9	132·3	118·1	121·6	113·4	104·1	98·4	42·3	45·5	—	24·3	11·8
= Hay with 14·3 per cent. water	190·6	181·1	170·1	128·2	154·4	137·8	141·9	132·3	121·4	114·8	49·4	53·1	—	28·3	13·8
Containing albuminoïds	14·63	15·60	12·59	11·53	12·98	8·69	10·53	10·06	9·02	7·34	3·53	4·50	—	3·01	2·84
Percentage of total N non-albuminoïd	26·6	26·9	31·8	28·6	29·5	36·1	27·3	28·9	22·5	26·1	32·9	28·7	28·8	18·2	14·5
Percentage of total albuminoïds, digestible	35·9	42·4	51·8	46·4	54·0	49·2	43·6	44·4	49·2	50·7	46·1	46·2	46·7	55·2	66·5
Albuminoïd ratio: 1 to	5·4	4·6	5·3	4·9	5·1	6·6	6·4	5·9	5·6	7·7	6·4	4·9	5·7	3·9	1·9
Comparative value, cocksfoot 1st cut = 100	100	106	103	116	113	97	104	106	101	104	106	108	106	124	201
Value of produce	1634	1645	1505	1276	1495	1146	1265	1202	1052	1023	448	491	—	301	237

II.—*Third Cutting of Portions A on October 12th.*

Composition of the fresh herbage.	Cocksfoot.	Meadow fox-tail.	Tall fescue.	Meadow fescue.	Sweet vernal.	Golden oat grass.	Timothy.	Perennial rye grass.	Wood meadow grass.	Rough-stalked meadow grass.	Crested dogs-tail.	Hard fescue.	Average of 12 grasses.	Fine-leaved sheeps' fescue.	Perennial red clover.
Water	77·85	72·87	74·93	75·06	75·97	75·04	71·26	77·75	72·77	68·11	68·23	71·20	73·42	69·50	80·94
Digestible albuminoïds	1·97	2·35	2·12	2·24	1·96	2·03	2·02	1·84	1·65	1·67	2·14	2·44	2·04	3·01	1·81
Indigestible albuminoïds	1·54	2·05	1·46	1·85	1·72	1·55	2·14	1·26	2·08	1·30	1·80	2·14	1·74	2·10	1·77
Non-albuminoïd N × 6·25	0·27	1·14	0·44	0·83	0·49	0·96	0·77	0·46	0·90	0·53	0·25	1·06	0·67	1·20	0·67
Fat, wax, and chlorophyll	1·16	1·51	1·36	1·26	1·24	1·13	1·65	1·26	1·15	1·33	1·57	1·48	1·34	1·80	0·95
Extractive matter free from nitrogen	8·66	11·93	11·20	11·23	12·17	11·46	13·61	10·17	12·31	16·50	17·42	12·45	12·43	12·18	9·27
Ash	2·91	2·88	3·03	2·89	2·56	2·85	2·83	2·44	3·40	4·64	3·24	2·96	3·05	3·69	1·81
Woody fibre	5·64	5·27	5·46	4·64	3·89	4·98	5·72	4·82	5·74	5·92	5·35	6·27	5·31	6·52	2·78
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Weight of green grass	205	83	98	84	69	162	54	125	86	25	18	60	—	54	79
Containing dry matter	45·4	22·5	24·6	20·9	16·6	40·4	15·5	27·8	23·4	8·0	5·7	17·3	—	16·5	15·1
= Hay with 14·3 per cent. water	53·0	26·2	28·7	24·4	19·4	47·1	18·1	32·4	27·3	9·3	6·6	20·2	—	19·3	17·6
Containing albuminoïds	7·20	3·64	3·51	3·43	2·54	5·79	2·24	3·87	3·20	0·75	0·71	2·74	--	2·77	2·83
Percentage of total N non-albuminoïd	7·1	20·6	10·9	16·9	11·7	21·2	15·7	12·9	19·4	15·1	5·9	18·8	14·7	19·0	15·7
Percentage of total albuminoïds, digestible	56·1	53·4	59·3	54·8	53·3	56·8	48·6	59·5	44·3	56·2	54·3	53·3	54·1	58·9	50·6
Albuminoïd ratio, 1 to	2·8	3·1	3·5	3·1	3·6	3·5	3·7	3·7	3·6	6·0	4·8	3·0	3·6	2·7	2·9
Comparative value, cocksfoot 1st cut = 100	137	148	136	149	146	140	137	136	129	112	131	145	137	150	164
Value of produce	621	333	334	311	242	565	212	378	302	90	75	251	—	247	248

III.—*First Cuttings of Portions B on July 13th.*

Composition of the fresh herbage.	Cocksfoot.	Meadow foxtail.	Tall fescue.	Meadow fescue.	Sweet vernal.	Golden oat grass.	Timothy.	Perennial rye grass.	Wood meadow grass.	Rough-stalked meadow grass.	Crested dogs-tail.	Hard fescue.	Average of 12 grasses.	Yarrow.	Perennial red clover.	Dutch clover.	Alsike clover.
Water	70·39	68·89	65·56	68·36	64·03	60·95	68·48	69·74	61·12	65·19	67·29	67·78	66·48	83·14	85·38	81·72	82·60
Digestible albuminoids	0·46	0·65	1·15	0·42	0·68	1·29	1·28	1·16	1·69	1·04	1·36	2·74	1·43	1·56	1·96	2·80	2·12
Indigestible albuminoids	0·74	0·65		0·81	1·08												
Non-albuminoid N × 6·25	0·09	0·23	0·27	0·32	0·35	0·75	0·46	0·16	0·99	0·42	0·52	0·98	0·46	0·55	0·76	0·42	1·06
Fat, wax, and chlorophyll	0·57	1·17	0·59	0·45	1·39	0·82	0·47	0·64	0·70	0·81	0·38	1·10	0·76	0·60	0·55	0·73	0·47
Extractive matter free from nitrogen	13·20	13·35	17·14	15·87	17·09	20·35	16·51	16·09	18·99	17·76	15·42	13·75	16·29	8·92	6·36	8·65	7·66
Ash	2·42	3·30	2·45	2·05	3·32	2·85	2·03	2·35	3·00	3·23	2·27	2·98	2·69	2·03	1·41	1·82	1·42
Woody fibre	12·13	11·76	12·84	11·72	12·06	12·99	10·77	9·86	13·51	11·55	12·76	10·67	11·89	3·30	3·58	3·86	4·67
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Weight of green grass	1284	617	921	830	789	485	789	949	396	600	548	189	—	—	589	150	756
Containing dry matter	380·3	191·9	317·3	262·6	283·9	189·4	248·6	287·2	153·9	208·9	179·3	60·9	—	—	86·1	27·4	131·5
= Hay with 14·3 per cent. water	443·7	223·9	370·2	306·4	331·3	221·0	290·1	335·2	179·6	243·8	209·2	71·1	—	—	100·5	31·2	153·4
Containing albuminoids	15·43	8·02	10·62	10·19	10·82	6·25	10·09	10·97	6·77	6·27	7·47	5·18	—	—	11·53	4·20	16·04
Percentage of total N non-albuminoid	7·4	15·0	19·1	20·8	16·8	37·0	26·5	12·4	37·0	28·4	27·6	26·3	22·9	26·1	27·9	12·9	33·8
Percentage of albuminoids, digestible	38·2	50·0	—	34·3	38·9	—	—	—	—	—	—	—	40·3	—	—	—	—
Albuminoid ratio: 1 to	11·9	12·1	15·0	13·7	11·3	17·1	13·6	15·0	12·1	18·6	11·9	5·8	13·1	6·3	3·7	3·5	3·9
Comparative value, cocksfoot, 1st cut = 100	70	81	73	74	82	77	79	78	80	73	74	100	78	115	131	144	125
Value of produce	2662	1554	2316	1943	2328	1458	1964	2241	1231	1525	1326	609	—	—	1128	395	1644

IV.—*Total Produce for the Season of Portions A.*

	Cocksfoot.	Meadow fox-tail.	Tall fescue.	Meadow fescue.	Sweet vernal.	Golden oat grass.	Timothy.	Perennial rye grass.	Wood meadow grass.	Rough-stalked meadow grass.	Crested dogs-tail.	Hard fescue.	Fine-leaved sheeps' fescue.	Perennial red clover.
1st cutting, June 3rd	994	900	786	582	784	576	610	636	385	437	182	173	82	89
2nd cutting, August 25th	962	646	573	591	504	550	508	293	322	338	303	279	233	2136
3rd cutting, October 12th	205	83	98	84	69	162	54	125	86	25	18	60	54	79
Total weight green grass	2161	1629	1457	1257	1357	1288	1172	1054	793	800	503	512	369	2304
Containing dry matter	443·8	382·9	308·8	322·7	318·5	359·6	310·7	220·1	246·7	224·6	187·0	139·9	109·3	430·6
= Hay with 14·3 per cent. water	517·9	446·7	360·0	376·5	371·7	419·5	362·5	256·8	287·8	262·0	218·2	163·3	127·5	502·5
Containing albuminoïds	37·40	33·42	26·19	23·54	25·82	23·28	20·49	18·64	20·68	16·57	11·47	13·99	12·81	47·94
Value of produce	4300	3805	3110	3160	3247	3320	2918	2242	2439	2295	1676	1505	1295	5047

V.—*Total Produce for the Season of Portions B.*

	Cocksfoot.	Meadow fox-tail.	Tall fescue.	Meadow fescue.	Sweet vernal.	Golden oat grass.	Timothy.	Perennial rye grass.	Wood meadow grass.	Rough-stalked meadow grass.	Crested dogs-tail.	Hard fescue.	Perennial red clover.	Dutch clover.	Alsike clover.
1st cutting, July 13th	1284	617	921	830	789	485	789	949	396	600	548	189	589	150	756
2nd cutting, September 13th	371	183	292	203	289	328	189	318	303	199	104	166	866	—	—
3rd cutting, October 12th	11	2	6	2	7	3	1	12	—	—	2	7	10	—	—
Total weight green grass	1668	802	1219	1035	1085	816	979	1279	699	799	654	362	1465	150	756
Containing dry matter	462·7	235·3	399·1	314·5	353·0	300·4	301·9	363·2	277·5	261·3	208·8	110·6	250·2	27·4	131·5
= Hay with 14·3 per cent. water	539·8	274·5	465·7	366·9	411·9	350·4	353·8	423·9	323·8	304·9	243·6	129·1	292·0	31·2	153·4
Containing albuminoïds	22·46	12·11	16·50	13·84	16·21	12·35	13·93	17·57	13·48	9·44	9·87	9·33	29·54	4·20	16·04
Value of produce	3449	2000	3092	2450	3021	2429	2479	3018	2380	2023	1629	1103	3115	395	1644

grasses cut at the same time. The clovers were affected a good deal by the winter's frost, the perennial red being the only one that yielded samples at all the cuttings. J. M. H. M.

Composition of White Mustard during Growth. By TROSCHKE (*Bied. Centr.*, 1886, 395—397).—The periods when examination of the composition of white mustard plants was made, were (I) before blooming, (II) at commencement of bloom, (III) full bloom, and (IV) at end of bloom.

The composition of the air-dry plant was as follows:—

	Period			
	I.	II.	III.	IV.
Water	16·0	16·0	16·0	16·0
Ash	8·9	7·1	6·1	5·5
Fibre	20·1	26·9	31·3	37·2
Fat	3·0	2·5	2·9	2·7
Crude protein	14·0	10·2	8·7	6·8
Pure albuminoïds	10·2	7·9	7·4	6·5
Extractives	38·0	37·3	35·0	31·8

As a fodder, mustard may be classed during the period I with good red clover, during later periods with meadow hay. The third period is the most advantageous for using mustard as green fodder, for then the absolute quantity of fat and nitrogen is largest. E. W. P.

Comparative Yield and Composition of Turnips Grown with Different Manures. By D. WILSON (*Trans. Highland and Agric. Soc. Scot.*, 1884, 304—324; 1885, 207—241).—These papers contain the results of four years of experiment at Killearn, Stirlingshire, the turnips being grown in 1882 and 1883 on stiff loam resting on the boulder clay, in 1884 on newly reclaimed moorland, and in 1885 on good free turnip soil in poor condition. The experiments each year comprised 28 plots of $\frac{1}{20}$ acre symmetrically arranged, and included a manurial analysis of the soil on Ville's principle of omitting all the constituents in turn from a complete artificial manure, a comparison between dissolved and undissolved phosphates, one between a complete artificial manure and farmyard manure, and one between artificial manures only, and a less quantity of the same manures supplemented with farmyard manure. The 1884 crop, as being exceptionally suitable, was chosen for a full analysis of the root in order to bring out the effect, if any, of the different manurial applications on the composition of the turnips. The conclusions arrived at from the whole series of experiments are the following:—

Sodium nitrate without phosphates as often decreased as increased the crop. With phosphates, it produced a regular increase of 20 per cent., so that the application pays best when the crop is a large one. Sodium nitrate does not bring the plant sooner to the hoe, and should be applied as a top dressing to the young plant. Potash salts, at the rate of 50 lbs. K_2O per acre, paid on only one of the experimental soils; it produces such different results on different soils that it should

only be used after experiment has proved it to be required by the particular soil to which it is proposed to apply it. Phosphoric acid is the necessary manure for turnips on nearly all soils; without it, the poorest soils produced roots the size of radishes, and the others only about a third of a crop. Sodium nitrate with dung repaid the outlay only in one season, when the crop was a very large one. Potash salts with dung decreased the crop in three out of the four seasons. Ground coprolites with dung had practically no effect on the crop. If 10—13 tons per acre of good dung be used the only addition that will repay the outlay is 3—5 cwt. superphosphate, or some other easily assimilated phosphate. Superphosphate, tried against an equal money value of ground coprolites, produced a greater increase of crop every year, the excess varying from 3 to 21 per cent., and averaging 10 per cent. Contrary to expectation, the superphosphate plots also bore the best crop the following season. Superphosphate every season brought the turnips sooner to the hoe. Steamed bone flour gave as good a crop as superphosphate; ordinary bone meal did not. Dung with artificials against no dung but more artificials produced better crops in three years out of the four; it is unlikely that dung could be used to greater advantage for any other crop.

Large turnips being less mature at the same date than smaller ones, contain more water, and are generally in other respects somewhat less nourishing; but if the turnips are of moderate size, and the growing season has been of average length, their composition is not much affected by the manures by which they have been grown. Differences of seed, climate, and soil, as affecting the conditions of maturity, affect the composition much more than differences of manure. So far as the differences due to manure can be discerned, concentrated nitrogenous manures, like sodium nitrate and ammonium sulphate, decrease the quality of turnips, especially when applied in excess of the other elements of plant food. Superphosphate produces bulbs richer in sugar than ground mineral phosphate. The manurial value of turnips grown by dung was considerably greater than when grown by artificials. A comparison of these analyses with similar ones made by Aitken of turnips grown at Pumpherston shows that the latter turnips had a decidedly higher feeding value, since a greater proportion of the nitrogen was albuminoïd. This is accounted for by the fact of their ripening earlier at Pumpherston than at Killearn. The average composition of the turnips from 27 plots grown at Killearn (1884) was as follows:—

Average weight of each bulb	25·4 oz.
Percentage of dry matter in fresh turnips	8·91
Composition of 100 parts dry matter :—	
Albuminoïds	6·06
Non-albuminoïd N × 6·25	6·76
Sugar	52·95
Extractive matter free from nitrogen	15·23
Ash	7·47
Fibre	11·54
Total nitrogen	2·056
Percentage of total nitrogen albuminoïd	47·3

J. M. H. M.

Relations between the Density, the Richness in Sugar, and the Purity of the Juice of Sugar-beet. By PAGNOUL (*Ann. Agronom.*, **12**, 221—225).—The author gives a new set of tables constructed from the results of nearly 1100 analyses, each analysis representing lots of 40—50 roots, samples of deliveries representing very various conditions of seed, manuring, soil, and culture. The roots after being washed and deprived of the tops, were cut into quarters longitudinally, and one quarter of each root taken for pressing. The whole sample of 40—50 roots thus furnished several litres of juice, with which the several determinations were made, after defecating it by crushing with it in a mortar 4 grams of lead subacetate, and then 5—8 decigrams sodium thiosulphate, and filtering. The first column in the table contains the degree of density, and the third column the mean richness in sugar as determined by analysis, the second column recording the number of analyses from which this figure is deduced. The curve, plotted from these results, connecting the richness with the density is very regular between the densities 5·1 and 6·6, where each determination represents the mean of a large number of analyses. Above and below these densities, however, the number of available analyses is much fewer, and the curve consequently more irregular and less trustworthy. In the fourth column of the table, a correction has been attempted by substituting for the figures derived from these few analyses those obtained by prolonging the regular portion of the curve obtained by plotting the medium mean densities. Between the densities 5·1 and 6·2 these corrected figures are of course identical with the actual ones; above and below these limits there is a slight difference.

The next column contains the weight of pure sugar necessary to give solutions of the observed densities, and the sixth column, containing the numbers got by subtracting the sugar really in the juice from these quantities of pure sugar, gives a measure of the impurities of the juice. The measure of purity in the seventh column is obtained by dividing the pure sugar column by the sugar actually present. The eighth column contains the coefficients by which each observed density must be multiplied in order to give the actual richness in sugar; this coefficient varies from 1·83 to 2·29, and the figure 2·00 is only correct for densities in the immediate neighbourhood of 4·8.

Density.	No. of analyses.	Sugar per decilitre. Mean found.	Sugar per decilitre. Mean corrected.	Sugar in a pure solution.	Non-sugar of juice.	Purity.	Coefficient of richness.	Sugar per cent. of roots.
4·1	0	—	7·5	10·6	3·1	71	1·83	6·9
4·2	0	—	7·8	10·9	3·1	72	1·85	7·1
4·3	0	—	8·1	11·1	3·0	73	1·88	7·4
4·4	3	8·4	8·4	11·4	3·0	74	1·91	7·7
4·5	3	8·9	8·7	11·7	3·0	75	1·93	7·9
4·6	3	9·2	8·9	11·9	3·0	75	1·94	8·1
4·7	4	9·2	9·3	12·2	2·9	76	1·98	8·4
4·8	5	10·0	9·6	12·4	2·8	77	2·00	8·7
4·9	11	9·9	9·9	12·7	2·8	78	2·12	9·0
5·0	15	10·3	10·3	13·0	2·7	79	2·06	9·3
5·1	38	10·4	10·6	13·2	2·6	80	2·07	9·5
5·2	43	10·9	10·9	13·5	2·6	80	2·09	9·8
5·3	48	11·2	11·2	13·7	2·5	81	2·11	10·1
5·4	52	11·4	11·5	14·0	2·5	82	2·13	10·3
5·5	82	11·9	11·9	14·3	2·4	83	2·16	10·7
5·6	72	12·1	12·1	14·5	2·4	83	2·16	11·0
5·7	70	12·4	12·4	14·8	2·4	84	2·17	11·1
5·8	74	12·7	12·7	15·1	2·4	84	2·19	11·4
5·9	72	13·0	12·9	15·3	2·4	84	2·19	11·6
6·0	76	13·2	13·2	15·6	2·4	85	2·20	11·8
6·1	67	13·4	13·4	15·8	2·4	85	2·20	12·0
6·2	65	13·7	13·7	16·1	2·4	85	2·20	12·2
6·3	63	13·9	13·9	16·4	2·5	85	2·20	12·4
6·4	54	14·1	14·1	16·6	2·5	85	2·20	12·6
6·5	28	14·4	14·4	16·9	2·5	85	2·21	12·8
6·6	22	14·6	14·6	17·1	2·5	85	2·21	13·0
6·7	9	14·7	14·9	17·4	2·5	86	2·22	13·2
6·8	16	14·8	15·2	17·7	2·5	86	2·23	13·6
6·9	17	15·0	15·4	17·9	2·5	86	2·23	13·8
7·0	7	15·3	15·7	18·2	2·5	86	2·24	13·9
7·1	5	15·5	15·9	18·4	2·5	86	2·24	14·1
7·2	4	15·2	16·2	18·7	2·5	87	2·25	14·3
7·3	8	15·8	16·5	19·0	2·5	87	2·26	14·5
7·4	4	16·2	16·7	19·2	2·5	87	2·26	14·7
7·5	4	16·8	16·9	19·5	2·6	87	2·26	14·9
7·6	1	15·5	17·2	19·8	2·6	87	2·26	15·1
7·7	1	16·8	17·4	20·0	2·6	87	2·26	15·3
7·8	0	—	17·7	20·3	2·6	87	2·26	15·5
7·9	1	18·4	17·9	20·5	2·6	87	2·26	15·7
8·0	1	17·9	18·1	20·8	2·7	87	2·26	15·9
8·1	1	18·8	18·4	21·1	2·7	87	2·27	16·1
8·2	1	19·6	18·6	21·3	2·7	87	2·27	16·3
8·3	0	—	18·9	21·6	2·7	87	2·28	16·5
8·4	2	18·1	19·1	21·8	2·7	88	2·28	16·7
8·5	1	17·3	19·4	22·1	2·7	88	2·28	17·0
8·6	1	18·8	19·7	22·4	2·7	88	2·29	17·2
8·7	1	19·1	19·9	22 6	2·7	88	2·29	17·4
8·8	2	19·8	20·2	22·9	2·7	89	2·29	17·6

The last column contains the percentage of sugar in the roots cal-

culated on the supposition that the weight of the juice is always $\frac{95}{100}$ of the total weight of the root.

The numbers contained in the table are true for the average of a number of deliveries of roots giving the same density, but not for any single delivery; the 76 analyses, for instance, from which the average richness of juice of density 6·0 was obtained, gave numbers for the actual richness varying from 11·9 to 14·3. J. M. H. M.

Oxidation of Ammonia in Water and Soils. By J. Uffelmann (*Bied. Centr.*, 1886, 362—363).—The author considers that the oxidation of ammonia is not wholly dependent on the presence of microbes, and he finds that the oxidation takes place very much more slowly, even when microbes are present, than is generally supposed. The absorption of atmospheric nitrous acid or ammonium nitrite by water greatly affects the percentage of nitrite found in the water. Experiments are quoted, in which although microbes were present, the formation of nitrous acid from ammonia did not occur. The soil when moist certainly has the power of absorbing nitrites from the air, but it cannot oxidise ammonia when sterilised. E. W. P.

Analytical Chemistry.

Witt's Filtering Apparatus. By A. Bornträger (*Ber.*, **19**, 1690).—A claim of priority.

Microscopic Analysis of Minerals. By T. H. Behrens (*Rec. Trav. Chim.*, **5**, 1—33).—This paper contains a description of methods used for the analysis of small fragments of minerals with the aid of the microscope, based on the detection of the various constituents by conversion into various compounds, the crystallographic forms or appearance of which are well known. The mineral is dissolved in hydrofluoric acid, or an acidified solution of ammonium fluoride, and the fluorides converted into sulphates under such conditions that the fluosilicates and fluoaluminates only remain unaltered. Then in the concentrated solution obtained, the calcium is detected in the form of sulphate, the potassium as the platinochloride, sodium as a double sulphate of cerium and sodium, lithium as sulphate after separation of the calcium sulphate, and barium and strontium also as sulphates. The double phosphate serves to indicate the presence of magnesium, and an alcoholic solution of alizarin, that of aluminium. For the detection of chlorine, mercurous is preferable to silver chloride; for fluorine, the best reagent is sodium chloride, the fluoride being previously converted into a silicofluoride. Test analyses are given, which were made with 0·0002 gram of tourmaline, of an apophyllite, a boracite, and other minerals. V. H. V.

Indirect Estimation of Fluorine. By S. Bein (*Chem. Centr.*, 1886, 330).—The author converts the fluorine (in native fluorides) into silicon tetrafluoride, and decomposes the latter with water; the resulting silica is collected and weighed; the weight multiplied by 5·494 gives the quantity of fluorine.

Elaborate details of the method are given, the observance of which is essential to success. C. F. C.

Estimation of Sulphur and Halogens in Organic Compounds. By P. Klason (*Ber.*, **19**, 1910—1913).—An ordinary combustion-tube drawn out and bent down at the further end is provided with three rolls of platinum gauze or thin foil, each 5 cm. long, placed at short distances from one another, the third being nearly in the middle of the tube. In starting a combustion, the first platinum roll is heated, and a current of oxygen saturated with nitrous fumes is passed by means of a long thin tube beyond the boat containing the substance; at the same time air is passed in from the end of the combustion-tube; thus that part of the tube as far as the boat is kept full of air, whilst the part containing the platinum rolls is filled with oxygen saturated with nitrous fumes. The combustion is then continued in the usual manner, the oxygen being passed in at such a rate that red fumes are always visible. In the case of sulphur estimations, the bent end of the tube merely dips into water contained in a flask, and the sulphuric acid is precipitated with barium chloride or titrated. With substances containing iodine, the product is passed into aqueous sulphurous acid. It the case of bromine or chlorine compounds, the gas passes first into a small flask containing silver nitrate, and then into a large flask containing some ammonia. It was found that only a trace of halogen passed into the ammonia.

In the combustion of substances little acted on by nitric acid, air need not be used; oxygen laden with nitrous fumes is passed through the whole tube. With volatile substances it is convenient to place a boat containing fuming nitric acid between the first and second platinum rolls. N. H. M.

Volumetric Estimation of Sulphur in Sulphides. By F. Weil (*Compt. rend.*, **102**, 1487—1489).—The mineral, such as galena blende or stibnite, is decomposed by hydrochloric acid, and the evolved hydrogen sulphide is absorbed in a standard ammoniacal solution of copper. The copper solution is filtered or made up to a definite bulk and allowed to settle, and the excess of copper is determined in an aliquot portion by means of standard stannous chloride, after acidifying with hydrochloric acid. If some fragments of zinc are added, the hydrogen which is evolved expels the last traces of hydrogen sulphide, and the zinc also facilitates the decomposition of such minerals as galena. C. H. B.

Volumetric Estimation of Sulphurous Acid. By C. Blarez (*Compt. rend.*, **103**, 69—71).—Sulphurous acid cannot be titrated with litmus, sulphofuchsine, or Poirrier's soluble blue C4B, as indicators, nor with ammonia or baryta as standard alkali. With helian-

thin and with cochineal, it behaves as a monobasic acid, and with phenolphthaleïn, as a bibasic acid, so that with the first two indicators 1 c.c. of decinormal alkali is equivalent to 0·0064 of sulphurous anhydride, but to 0·0032 with phenolphthaleïn. Some of the results obtained were as follows, in grams per litre:—

With standard iodine.....		3·840	9·884	4·000
With alkali and	phenolphthaleïn.	3·776	9·824	4·000
	cochineal	3·792	9·788	4·000
	helianthin.....	3·795	9·737	4·000

Sulphurous acid can be estimated in presence of another monobasic or polybasic acid, provided that the latter shows its full basicity with cochineal or helianthin. Two titrations are made; the first with cochineal or helianthin, the second with phenolphthaleïn, and the difference in c.c. of alkali, multiplied by 0·0064, gives the amount of free sulphurous anhydride.

Acid sulphites, containing an excess of free acid, are acid to cochineal or helianthin, and the excess of acid can be determined by means of these indicators. Pure acid sulphites are neutral to cochineal or helianthin, but are acid to phenolphthaleïn, and can be titrated with this indicator. Normal sulphites are alkaline to cochineal or helianthin, but neutral to phenolphthaleïn, and can be titrated with either of the two first indicators and decinormal hydrochloric acid.

With an intermediate sulphite, a titration is first made with phenolphthaleïn as indicator. The same volume of solution is mixed with excess of standard hydrochloric acid and titrated back with cochineal or helianthin as indicator. The sum of the volume of alkali used in the first titration and the quantity of acid really used in the second titration gives the amount of sulphurous acid in the volume of solution taken. The amount of alkali required to convert the sulphurous acid into normal sulphite is given by the first titration, and from these data the exact composition of the sulphite can be calculated.

C. H. B.

Mitscherlich's Test for Phosphorus. By K. Polstorff and J. Mensching (*Ber.*, **19**, 1763—1764).—Lecco has lately shown (this vol., p. 743) that in employing Mitscherlich's test in toxicological investigations, the luminosity of the phosphorus vapour is destroyed if mercuric chloride is present in the distilling flask. The author now finds that this is also the case with other mercury salts. Cupric salts do not produce this effect. The author therefore concludes that a part of the mercuric chloride becomes volatilised, and this then oxidises the phosphorus present in the vapour. The reduced mercury passes over into the distillate, together with a small quantity of the phosphoric acid formed; whilst the greater part of the latter falls back into the distilling flask. If any other mercuric salt than the chloride is present, the latter appears to be formed by double decomposition with the other chlorides; whilst mercurous chloride is probably decomposed by the albuminoïds present into mercury and mercuric chloride.

L. T. T.

Estimation of Arsenic in Ores, Mattes, and Metallic Copper. By G. W. Lehmann and W. Mager (*Chem. News*, **53**, 302).—Pearce's method is recommended as the most trustworthy and convenient for determining small quantities of arsenic. The finely powdered substance is fused with six times its weight of equal parts of sodium carbonate and potassium nitrate, extracted with hot water, filtered, acidified with nitric acid, boiled, allowed to cool, silver nitrate added, the whole neutralised with ammonia, and the silver determined in the precipitated silver arsenate. When analysing copper, the metal is dissolved in nitric acid and mixed with a small quantity of iron sulphate also dissolved in nitric acid; this solution is then precipitated with ammonia, the precipitate is washed, dried, and examined as above. The method answers well even in presence of lead, antimony, and aluminium salts. D. A. L.

Determining Small Quantities of Sodium Chloride in Presence of Potassium Chloride. By G. Laube (*Chem. Centr.*, 1886, 246).—The salt is dissolved in twice its weight of water, and to the solution 4 vols. of absolute alcohol is added. When cold, a measured quantity of the solution is drawn off, and the alkalis determined as described by Röttger and Precht (Abstr., 1885, 1263). C. F. C.

Estimation of Caustic and Carbonated Alkali in Presence of each Other. By H. J. Phillips (*Chem. News*, **54**, 28).—The sample for analysis is dissolved in water which has been recently boiled to drive off any free carbonic anhydride it may contain, the solution is treated with sufficient barium chloride to precipitate all combined carbonic anhydride, and the whole heated and allowed to cool. Normal hydrochloric acid is run in until the hydroxide is neutralised (when the colour of phenolphthaleïn disappears), and the volume is noted; more acid is then run in in excess of that required to dissolve the barium carbonate, and the excess is titrated back with normal sodium carbonate. D. A. L.

Detection of Calcium in Presence of Strontium. By C. L. Bloxam (*Chem. News*, **54**, 16).—When strontium chloride is precipitated by excess of sulphuric acid, the strontium remaining in solution is not precipitated by ammonia and arsenic acid, whereas under similar circumstances calcium gives a crystalline precipitate of calcium ammonium arsenate. By this means 1 part of calcium can be easily detected in presence of 100 of strontium, and by concentrating the liquid after the precipitation of the strontium, 1 in 500 can be detected. In fact, a solution containing Ca in 113,235 of water gave a distinct crystalline precipitate. D. A. L.

Volumetric Determination of Copper with Potassium Cyanide. By A. H. Lord (*Chem. Centr.*, 1886, 204).—The solution of cyanide is standardised as follows:—0·3—0·5 gram copper is dissolved in nitric acid (5 c.c.) and heated till no more red fumes appear; the solution is diluted and 10 c.c. strong ammonia added. This solution is titrated until the end reaction is approached; then diluted to

180 c.c., previously to adding the last portions of cyanide. The reaction is complete when a blue coloration is observed.

The cyanide solution should be preserved in a dark place, and covered with liquid paraffin.

The method of preparing the solution for titration from ores and mixtures containing copper is necessarily determined by their composition. C. F. C.

Detection of Mercury. By G. Kroupa (*Chem. Centr.*, 1886, 250).—Eschka's test for mercury involves confirmatory examination of the mirror produced upon the gold. For this the author uses a fragment of iodine. This placed upon the surface to be tested, produces a scarlet coloration (HgI_2) immediately beneath, with a surrounding zone of a yellowish-green colour (Hg_2I_2). In the case of minute quantities, the reaction should be observed under a lens.

C. F. C.

Quantitative Chemical Analysis by Electrolysis. By T. Moore (*Chem. News*, **53**, 209—210).—When solutions containing either iron, cobalt, nickel, zinc, cadmium, aluminium, chromium, or manganese, are treated with phosphoric acid and ammonium carbonate, and are electrolysed, the first five are completely precipitated, chromium forms a soluble chromate, manganese is partially deposited as oxide on the other electrode, whilst the aluminium is unaltered. For separate determinations of the first five, the following plan answers well: The slightly acid solution of ferric (or other) *sulphate* or *chloride* is treated with a solution containing 15 per cent. of glacial phosphoric acid until the yellow colour disappears, ammonium carbonate is added in large excess, and the whole warmed gently until the solution is clear. On electrolysing the hot solution (70°) with a current equal to 1200 or 1300 c.c. mixed gases per hour, the iron (or other metal) is deposited rapidly and completely. A current equal to 100 to 300 c.c. of mixed gases per hour is sufficient to effect the deposition of the zinc, whilst a current of 40 c.c., which gives no deposit with zinc, is strong enough for cadmium. A good solution for the electric deposition of either zinc or cadmium is prepared by precipitating the solution of a zinc or cadmium salt with sodium phosphate, dissolving the precipitate in potassium cyanide, and adding excess of ammonium carbonate. This solution when electrolysed at 80° with a current equal to 1000 c.c. of mixed gases per hour gives a rapid and complete deposit. Zinc is best deposited on silver-plated electrodes. For copper, the freshly precipitated sulphide dissolved in potassium cyanide, and mixed with excess of ammonium carbonate, is recommended. Manganese is best estimated by deposition as oxide on the positive electrode from a slightly acid solution of nitrate or sulphate; it is, however, interesting to note that a large proportion is deposited as metal by electrolysing with a powerful current a neutral solution containing a large excess of ammonium thiocyanate. For bismuth, sufficient tartaric acid is added to prevent precipitation of basic salt, the solution is rendered strongly alkaline with ammonia, mixed with considerable excess of glacial phosphoric acid, and electrolysed at first

with a weak (20 to 30 c.c. gas per hour) current, subsequently with a current = 450 c.c. gas. Tin is easily precipitated from either acid or alkaline glacial phosphoric acid solutions. An attempt to estimate arsenic as AsH_3 by electrolysing its acid solution in presence of zinc sulphate was not successful. D. A. L.

Separation of Metals by means of Oxalic Acid. By C. Luckow (*Chem. Zeit.*, **10**, 763—764 and 793).—The substance containing the mixture of metals is dissolved in a sufficiency of aqua regia, excess of a boiling solution of oxalic acid is added, the whole boiled, and allowed to subside. Subsidence is aided by the addition of ammonium chloride; the addition must, however, not be made when tin and antimony are to be determined electrolytically. Chromium, aluminium, tin, iron, antimony, and arsenic remain in solution if all or any of them are present. The precipitate and solution may be examined in the usual manner. In the presence of sufficient oxalic acid, solutions of stannic or antimonic chloride may be evaporated over a water-bath without any noteworthy loss of either metal by volatilisation, and the residue dissolves in water to a clear solution. Electrolytic methods, wherever convenient, are recommended. When solutions containing tin and antimony are electrolysed in presence of much oxalic acid, tin alone is precipitated; also when such solutions, or solutions acidified with hydrochloric acid, are electrolysed, using metallic mercury as a negative electrode, tin alone forms an amalgam. Both methods are useful for the separation of the two metals. D. A. L.

Quantitative Separation of Uranium from the Alkalis and Alkaline Earths. By G. Alibegoff (*Annalen*, **233**, 143—153).—Foullon has recently pointed out (*Jahrbuch Geolog. Reichanstalt*, **33**, 23) that the separation of uranium and calcium by means of ammonium sulphide does not yield correct results, as the precipitated uranium contains calcium carbonate and sulphate. He proposes to precipitate the calcium as oxalate in the presence of an excess of ammonium carbonate. The author finds that this method is preferable to the former, although it is not quite accurate; small quantities of uranium are carried down with the calcium oxalate. Uranium is most conveniently estimated by adding freshly precipitated mercuric oxide to the boiling solution of the uranium salt containing a few drops of ammonium chloride. The mixture is boiled for a few minutes, then cooled, and the precipitate washed by decantation with cold water containing a small quantity of ammonium chloride. If the solution contains a relatively large quantity of strontium or calcium, the precipitate must be boiled with water containing ammonium chloride. If magnesium is present, the solution must be boiled with ammonium chloride before the addition of the mercuric oxide. The dried precipitate is ignited in a platinum crucible, the temperature being gradually raised, and the crucible finally heated at the blowpipe. The residue consists of pure U_3O_8. W. C. W.

Detection and Estimation of Vanadium by Means of Oxycellulose. By G. Witz and F. Osmond (*Bull. Soc. Chim.*, **45**, 309—314).—Strips of the oxycellulose described by G. Witz (*Bull. Soc. Indus. Rouen*, 1882, 449) are immersed in the solution containing the vanadium salt for eight hours at 15°. They are washed, dried at 40°, and printed with the usual aniline-black mixture, to which, however, no hypovanadic chloride has been added; the colour is then developed in the oxidation chamber during a given time, and the amount of vanadium present in the solution examined is estimated by the depth of the black obtained. By this means, the presence of as little as 0·000001 milligram of vanadium in the form of hypovanadic chloride may be detected in 1 litre of water. The presence of 0·5 to 1·0 c.c. of a mineral acid, as also the presence of ammonium oxalate, altogether prevent the fixation of the vanadium by the fibre. Iron salts act similarly to vanadium salts in the formation of aniline-black, but the action is only $\frac{1}{5000}$ as strong. The chlorides, sulphates, and acetates of the alkalis and alkaline earths all diminish the sensibility of the reaction.

In the examination of a water for vanadium, the iron salts should first be removed, all the salts present converted into chlorides or sulphates, sufficient sodium acetate added to remove any excess of free mineral acid, and the process then conducted as above. The results obtained are approximately quantitative, the foreign salts present being constant.

The authors have detected the presence of vanadium in the drinking water of Creusot, and in the sulphurous mineral water of Saint-Honoré-les-Bains. It is not present in the mineral waters of Châtel Guyon, la Bourboule, Pouges, Royat, and Mont Doré. It was also absent from a sheep, the principal organs and bones of which were examined. A. P.

Electrolytic Estimations and Separations. By E. F. Smith and E. B. Knerr (*Amer. Chem. J.*, **8**, 206—211, compare Abstr., 1883, 1034).—From a solution of bismuth sulphate containing free sulphuric acid, the metal can be completely and rapidly deposited by the current, in the cold. The presence of ferrous, ferric, nickel, cobalt, and manganese salts do not interfere; neither do alumina, chromium, cadmium, uranium, or zinc compounds. The current gave 1 to 3·5 c.c. of electrolytic gas per minute, the time required varied from $\frac{1}{2}$ to 3 hours.

Mercury may be completely separated from solutions of the nitrate, in presence of a small amount of free nitric acid, in $\frac{1}{2}$ to $\frac{3}{4}$ hour with a current giving 4 c.c. of electrolytic gas per minute.

When separating zinc and cadmium in acetic acid solution, the current should not give more than 0·1 c.c. of gas per minute. In tartaric acid solution, the deposition of metal is very rapid at first; the last traces are, however, difficult to remove. H. B.

Two New Sugar Reactions. By H. Molisch (*Monatsh. Chem.*, **7**, 198—209).—When a small quantity of a sugar solution is mixed with two drops of an alcoholic solution of α-naphthol, and an excess

of strong sulphuric acid added, a deep violet coloration is at once obtained, and on dilution with water a bluish-violet precipitate is thrown down. This reaction is obtained with many of the carbohydrates—sucrose, lactose, dextrose, levulose, and maltose—but not with mannitose and allied carbohydrates. It is also given by most of the glucosides. With starch, cellulose, dextrin, &c., no reaction is given at first, but as these substances become broken down by the acid, the coloration begins to form: this can be best observed microscopically. Inulin gives the coloration at once. By means of this reaction, the author has easily identified 0·00001 per cent. sugar.

A solution of thymol used in place of the naphthol gives a deep red coloration, which on dilution with water gives at first a fine carmine coloration, and then a carmine flocculent precipitate. In all other respects it behaves like naphthol.

The test is of especial value for micro-chemical examinations, and proved of service in distinguishing the spherical crystals of inulin from those of hesperidin.

By means of these reactions, the author has established the correctness of the statement that normal urine always contains sugar, and even when diluted with 100 to 300 times its volume of water it still gives the colorations. The sugar of normal urine and that of diabetic urine can easily be distinguished by comparing the colorations produced in different states of dilution, diabetic urine giving a coloration when diluted with 600 times, or even more, its volume of water. G. H. M.

Detection of Salicylic Acid in Beer and Wine. By Röse (*Chem. Centr.*, 1886, 412).—The beer or wine is acidified with sulphuric acid, and shaken with its own volume of a mixture of equal parts of ether and light petroleum. The ethereal layer is filtered and distilled down to a few cubic centimetres. The residue is mixed whilst hot with a little water, then with a few drops of weak ferric chloride, and is filtered through a wet filter. If salicylic acid is present, the filtrate is violet coloured; 0·1 mgrm. per litre can be detected. Should the addition of ferric chloride produce a tannic acid reaction, it is necessary to reacidify, dilute, and again extract with the ether mixture. The second residue will give the reaction of salicylic acid, of which 0·2 mgrm. per litre can be detected even in wines containing much tannic acid. M. J. S.

Addition of Goat's Milk to Cow's Milk. By N. Gerber (*Bied. Centr.*, 1886, 419).—The adulteration of cow's with goat's milk cannot be detected by the lacto-densimeter, nor by estimation of fat, but the presence of goat's milk may be judged by the cream not rising. Cream does not form on goat's milk, and the presence of this milk prevents much of the cream rising on cow's milk. The presence of only 10 per cent. of goat's milk greatly reduces creaming.

E. W. P.

General and Physical Chemistry.

Electric and Thermic Properties of Salt Solutions. By J. Moser (*Monatsh. Chem.*, **7**, 273—279).—In this paper a summary is given of the author's publications on the electric constant of dilution, and the relation between it and the diminution of vapour-tension of salt solutions. As a suitable example to illustrate the relation between these electric constants, in which the ratio of the concentration of the solutions at the anode and kathode respectively is 1 : 2, the cases of lead acetate and nitrate and of zinc acetate and nitrate are selected. It is thus shown that the difference between these constants for the metallic and the non-metallic radicle is the same; so that in every series of four salts similarly related, ak, ak_1, a_1k, and a_1k_1, if $a + k$, $a + k_1$, and $a_1 + k$ be known, $a_1 + k_1$ can be calculated.

It further follows from the equations deduced from the theories put forward by the author and Helmholtz, that with a ratio of concentration 1 : 2, the electric constant of dilution α is a product of three factors, namely:—(1) $\alpha = Cb\,(1-n)$, in which C is a constant of the same value for every salt, b is the diminution of vapour-tension, and $1-n$ the transference value of the ions. If the transference value be unity, then (2) $\alpha_1 = Cb$. From equations (1) (2) $1-n = \frac{\alpha}{\alpha_1}$, but from the researches of Kohlrausch and of Hittorf, $1-n = \frac{v}{w+v}$, that is to say, the transference value of the anions is equal to the ratio between its molecular conductivity and the sum of the molecular conductivity of both ions. Hence $\frac{\alpha}{\alpha_1} = \frac{v}{w+v}$, or the electric constants of dilution are in the same ratio, and thus is expressed a relation between the electromotive force and resistance in this formula. V. H. V.

Equilibrium of Aqueous Solutions. The Existence of Acid Salts and Double Salts in Aqueous Solutions. By T. Thomsen (*J. pr. Chem.* [2], **34**, 74—91).—Landolt has shown that the acid tartrates of sodium and of ammonium in aqueous solution have a molecular rotation, which is the mean of the molecular rotations of the neutral salts and of the free acid, and from this he concludes that the acid salts do not exist in aqueous solutions, but are decomposed into a mixture of the free acid and of the basic salt. By molecular rotation is understood $[m]_D = m[\alpha]_D/100$; but solutions of only one strength were examined, and at one temperature. New determinations have therefore been made, using solutions of various strengths and at various temperatures, in the hope that an answer to the question as to the existence or non-existence in solution of the acid salts might be obtained.

The molecular rotation of tartaric acid has been previously deter-

mined (*J. pr. Chem.* [2], **32**, 216—218); that of sodium tartrate at 15° is $= 60{\cdot}75-0{\cdot}08314P-0{\cdot}001418P^2$; at 20° $= 60{\cdot}56-0{\cdot}04647P-0{\cdot}002216P^2$, and at 25° $= 61{\cdot}35-0{\cdot}08478P-0{\cdot}001594P^2$, where P varies from 9·20—36·77, and $= 60{\cdot}20 + 0{\cdot}06087P-0{\cdot}005198P^2$ at 30°, when P varies from 9·20—18·40. Solutions of hydrogen sodium tartrate of various strengths were examined at various temperatures, and the results found to be higher than those given by a mixture of the normal tartrate with tartaric acid, as calculated from the above numbers. The following are the differences:—

P.	15°.	20°.	25°.	30°.
12·70	—	—	—	2·15
10·16	—	—	1·42	1·27
8·89	—	1·26	0·70	0·89
7·62	1·45	1·12	0·95	1·14
6·35	0·68	0·86	0·13	0·23

Hence it is inferred that the acid salt is partially decomposed on dilution, and the more so the larger the amount of water present, and also by an increase in temperature. Schneider's determinations made with the acid malates of potassium, sodium, lithium, and ammonium lead to exactly similar conclusions (*Annalen*, **207**, 257).

Double Salts.—Landolt has shown that at 20° the molecular rotations of the double tartrates of the alkalis are the means of those of their component salts. The sodium potassium tartrate is now further examined at various temperatures, as the molecular rotations of the component tartrates vary in opposite directions considerably with the degree of concentration. For potassium tartrate $[m]_D$ at 15° $= 62{\cdot}28 + 0{\cdot}2091P-0{\cdot}001467P^2$; at 20° $= 62{\cdot}42 + 0{\cdot}2405P-0{\cdot}002449P^2$; and at 25° $= 62{\cdot}97 + 0{\cdot}2149P-0{\cdot}002240P^2$. The mean values of the two tartrates are found at all temperatures and at all concentrations to be equal to the values of the solutions of the double salt, and hence it is probable that even in the strongest solutions the sodium potassium tartrate is completely decomposed into the constituent salts.

H. B.

Inorganic Chemistry.

Production of Rich Phosphate of Lime in Connection with an Improvement of the Thomas-Process. By C. Scheibler (*Ber.*, **19**, 1883—1893).—In the modified process, the lime used to assist the removal of phosphorus from the iron is added by degrees, and the slag formed after each addition poured off; the quantity of lime added is only 12 per cent. instead of 18 to 20 per cent. In this way, two sorts of slags are obtained, the first containing most of the

phosphorus, and only a small quantity of iron; the second contains most of the iron which has become oxidised in the process, and only a small amount of phosphorus. The first forms an important material for manure, whilst the second is of value for the production of crude iron. N. H. M.

Behaviour of the Alkaline Earths and their Hydroxides towards Dry Carbonic Anhydride. By C. Scheibler (*Ber.*, **19**, 1973—1982).—The results of several experiments described in the paper point to the following conclusions:—

1. Dry carbonic anhydride combines neither with the anhydrous oxides of earth metals, nor with their monohydroxides, nor with the compound $Ba(OH)_2 + H_2O$.

2. When dry carbonic anhydride is passed over the hydroxides $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2 + H_2O$ at 100°, any excess of water present will be removed; and the gas thus moistened will act on the hydroxide with formation of carbonate. The hydroxide is, however, not completely converted into carbonate, even when 8 mols. H_2O are present.

3. The use of dry carbonic anhydride to remove water from alkaline earths, and to convert the earths into carbonate, does not work as an analytical method. N. H. M.

Mineralogical Chemistry.

The Tysnes Meteorite. By H. Reusch (*Jahrb. f. Min.*, 1886, *Beilage* **4**, 473—518).—At Midt-Vaage, on the eastern side of the island of Tysnes, 31 miles south-east of Bergen, there fell, on 20th May, 1884, between 8 and 9 P.M., a meteoric stone, weighing 18·96 kilos. In the immediate vicinity of the place of fall, a number of fragments were collected, amounting in all to 21·7 kilos. The meteorite in form resembles the quarter of a cylinder. It is covered with a black melted crust, never more than 0·5 mm. thick. The stone does not crumble like many other meteorites, but is tolerably hard. The characteristic of this meteorite is its remarkable brecciated structure. In a dark-grey ground-mass, there are scattered sharply angular fragments, lighter in colour. The stone is evidently a chondrite with brecciated structure; under the microscope, it is seen to consist essentially of bronzite, olivine, and iron, with a small quantity of magnetic pyrites.

In conclusion, the author compares this meteorite with three others which have fallen in Scandinavia, the Hessle meteorite, fallen 1st January, 1869, at 12.30 P.M.; the Stalldal meteorite, fallen 28th June, 1870, at 11.32 A.M.; and the Ski meteorite, fallen 27th December, 1848, in the evening. B. H. B.

Swedish Minerals. By M. Weibull (*Zeit. Kryst. Min.*, **12**, 90—91).—An abstract of the first part of this memoir has already been given (Abstr., 1886, 33). In the second part the author discusses the *knebelite* of Dannemora, and compares it with the iron knebelite of West Silfberg.

The inclusions in the knebelite are grains of magnetite and alteration products, amounting to about 5 per cent. On analysis the knebelite gave the following results:—

SiO_2.	FeO.	MnO.	MgO.	CaO.	Al_2O_3.	Total.
28·96	36·73	29·69	2·33	1·00	1·07	99·78

The chemical constitution is consequently $(FeMnMg)SiO_4$.

B. H. B.

Minerals from the Eruptive Rocks of the Cretaceous Formations of Silesia and Moravia. By E. M. Rohrbach (*Zeit. Kryst. Min.*, **12**, 86—87).—The teschenites contain, as primary constituents, plagioclase, augite, hornblende, biotite, olivine, apatite, titaniferous iron, magnetite, orthoclase, and titanite; and, as secondary constituents, analcime, natrolite, apophyllite, and other zeolites, calcite and aragonite, biotite, leucoxene, chloritic and serpentine-like substances, epidote, pyrites, and plagioclase. Nepheline is not present. The mineral hitherto thought to be nepheline appears to be apatite. Augite and hornblende are frequently intimately associated. The chemical composition of the augite (I), and the hornblende (II) from the teschenite of the Teufelsgrund are as follows:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Total.	Sp. gr.
I.	44·22	10·49	11·98	5·77	7·02	22·54	102·02	3·376—3·421
II.	36·91	16·30	5·28	12·27	8·83	16·91	96·50	3·364—3·370

B. H. B.

Magnetite from Scalotta. By A. Cathrein (*Zeit. Kryst. Min.*, **12**, 37—39).—The crystallographical characters of this variety of magnetite, notable for its richness in planes and for the occurrence of new forms, have already been described (*Zeit. Kryst. Min.*, **9**, 365). The author has now submitted crystals, as pure as possible, to analysis. The results were as follows:—

Fe_2O_3.	Cr_2O_3.	Al_2O_3.	FeO.	MnO.	MgO.	Total.
68·51	0·55	1·10	27·70	0·42	2·09	100·37

The formula for the Scallota magnetite, then, is—

$$(61Fe_2O_3)(\tfrac{1}{2}Cr_2O_3)(\tfrac{3}{2}Al_2O_3) + (55FeO)(1MnO)(7MgO);$$

the mineral analysed being a normal magnetite, free from titanium, with its ferric oxide partially replaced by chromium oxide and alumina; whilst magnesia and manganous oxide are isomorphically mixed with the ferrous oxide. B. H. B.

Organic Chemistry.

Action of Chlorine and Bromine on Organic Bromides and Iodides. By R. Meyer (*J. pr. Chem.* [2], **34**, 104—109).—*Preparation of Isopropyl Bromide from the Iodide.*—Bromine is gradually added to isopropyl iodide kept cool, one and a half times the theoretical quantity of bromine being used. The product is washed with soda solution and then fractionated. The yield of pure substance is 70 per cent. of the theoretical. The action of bromine on methyl and ethyl iodides exactly resembles the above.

Chlorine acts readily on isopropyl iodide, but further substitution products are also formed. Chlorine, however, does not act at all on isopropyl bromide; this is remarkable, as according to J. Thomsen, a considerable amount of heat is developed in similar cases: thus with primary propyl bromide, $C_3H_7Br + Cl = C_3H_7Cl + Br = +6910$, and also $C_3H_7I + Br = C_3H_7Br + I = +11910$. H. B.

Cyanuric Ethers. By A. W. Hofmann (*Ber.*, **19**, 2061—2083).—After referring briefly to his own researches and those of Olshausen (*Ber.*, **3**, 269), Mulder, Ponomareff (this vol., p. 216), and Claësson (this vol., p. 324), the author describes further experiments which he has carried out with the help of Dr. O. Rhousopoulos and Dr. E. A. Wülfing.

The authors find that normal trimethyl cyanurate is best prepared by Ponomareff's reaction (action of cyanuric chloride on sodium methylate), as the formation of bye-products which always takes place when cyanogen chloride, bromide, or iodide act on sodium methylate is entirely avoided. Trimethyl cyanurate melts at 135° (previously given as 132°), and boils at 265°, a little being at the same time converted into the isomeric isocyanurate. The normal cyanurate dissolves in cold concentrated hydrochloric acid, but is reprecipitated unchanged from the solution by alkalis. When boiled with hydrochloric acid, the ether yields methyl chloride and cyanuric acid; with alkalis, methyl alcohol and an alkaline cyanurate.

Fock has physically examined the crystals of several of the compounds obtained during this research, and his results are given in detail. Cyanuric chloride (m. p. 146°) crystallises in the monosymmetric system, the axial relations being $a : b : c = 1{\cdot}0176 : 1 : 1{\cdot}5010$ and $\beta = 83° 50'$; normal trimethyl cyanurate, rhombic system, long prisms, melting at 135°; normal trimethyl thiocyanurate, hexagonal system, m. p. 189°; trimethyl isocyanurate, m. p. 176°, monosymmetric system, $a : b : c = 1{\cdot}1606 : 1 : 0{\cdot}6092$, and $\beta = 69° 34'$. The author calls attention to the similarity in crystalline form between trimethyl cyanurate and trimethyl thiocyanurate. *Normal dimethyl-cyanuric acid*, $(CN)_3(OMe)_2OH$, obtained in small quantities in the preparation of trimethyl cyanurate, is best obtained by dissolving

2 grams of sodium in 15 c.c. of methyl alcohol, adding thereto 15 grams of trimethyl cyanurate, and heating the mixture in closed tubes at 100° for about 1½ hours. It forms small hexagonal scales, soluble in alcohol and water, insoluble in ether. The melting point varies between 160° and 180°, according as the temperature is raised quickly or slowly, partial decomposition taking place at the same time. This compound differs from cyanuric acid in being easily soluble in ammonia, from which solution it is reprecipitated by acids. The ammoniacal solution yields a rose-red salt with copper sulphate. Dimethylcyanuric acid may also be obtained by the action of sodium methylate on trimethyl thiocyanurate, sodium thiomethylate being also formed. This acid is isomeric with the substance previously described by the author as dimethyl cyanurate (Abstr., 1881, 822), but which he now proposes to call *dimethylisocyanuric acid*. The latter is decomposed by alkalis into carbonic anhydride, methylamine, and ammonia, thus differing from the normal cyanurates. When normal dimethylcyanuric acid is very gradually heated, it begins to soften at 165—170°, and at a slightly higher temperature melts suddenly to a liquid, which immediately begins to boil strongly and continues to do so for some seconds. This boiling appears to be caused by a great development of heat (the thermometer in the liquid rapidly rises to 320°) during the transformation of the normal into the iso-acid. When cool, the resulting mass is found to consist of dimethylisocyanuric acid, together with a little trimethyl isocyanurate; the latter is probably due to slight decomposition produced by the high temperature. The dimethyl acid can also be obtained by the action of methyl iodide on silver cyanurate; by the action of strong oxidising agents on trimethyl isocyanurate; and by the distillation of dimethylcarbamide. The yield in all cases is very small, but the formation is of theoretical interest. The acid crystallises in the monosymmetric system, and melts at 222°; it forms a crystalline *silver salt*, $C_6N_3H_9O_3Ag + \frac{1}{2}H_2O$.

Normal trimethyl cyanurate, when treated with cold ammonia, yields dimethyl amidocyanurate, $(CN)_3(OMe)_2NH_2$, described by Hofmann and Olshausen. The silver salt, $(CN)_3(OMe)_2NH_2,AgNO_3$, crystallises in quadrilateral plates. The *platinochloride* forms small scales, the *aurochloride* is also crystalline. The amidocyanurate melts at 217—220°, and is at the same time converted into the isomeric iso-compound, the same phenomena being observable as with dimethylcyanuric acid. When normal trimethyl cyanurate is heated with alcoholic or aqueous ammonia at 100° or above, decomposition takes place, melamine, and eventually ammeline and ammelide, being amongst the products.

Normal triethyl cyanurate, already described by Mulder, Claësson, and Ponomareff, is best prepared in the same way as the methyl-compound. It forms needles melting at 29—30°. It is less easily converted into the iso-compound, distilling at 270° unchanged, and only being transformed into its isomeride (described in 1849 by Nicklès and by Rammelsberg) by continued digestion with a reflux condenser. The iso-compound melts at 95°. A curious and interesting reaction is the conversion of normal trimethyl cyanurate into

normal triethyl cyanurate by digesting it with the equivalent quantity (3 mols.) of sodium ethoxide. Trimethyl thiocyanurate when similarly treated also yields triethyl cyanurate. Triethyl isocyanurate crystallises in small colourless prisms belonging to the rhombic system; $a : b : c = 0{\cdot}9719 : 1 : 0{\cdot}9325$, and melts at 95°. Normal diethylcyanuric acid, described by Mulder and by Ponomareff, is best prepared by the action of sodium ethoxide on trimethyl cyanurate, or the corresponding thio-compound. Differing from Mulder, the author obtained a rose-coloured *calcium salt*. This diethyl-compound has no definite melting point; it varies between 160—180°, the isomeride already described by Habich and Limpricht, and by Wurtz, being always formed. The latter compound forms hexagonal-rhombohedric-tetartohedric crystals, giving measurements $a : c = 1 : 0{\cdot}6271$. Diethyl amidocyanurate melts at 97° and resembles the dimethyl-compound. *Ethyl diamidocyanurate* is obtained when diethylamidocyanurate is allowed to remain with concentrated ammonia at the ordinary temperature. It melts at 190—200°, and apparently changes to the iso-compound. It forms a *silver salt* and a *platinochloride*, the latter being decomposed by water.

Similar compounds are formed in the propyl series. Normal tripropyl cyanurate melts at the ordinary temperature. It cannot be distilled under the ordinary pressure, but at 76 mm. it boils at 220°, and on continued heating is converted into the iso-compound, which was not, however, obtained in a crystalline form. Similar amyl-compounds appear to be obtainable.

Normal phenyl cyanurate, previously described by Hofmann and Olshausen, is best obtained by the action of sodium phenylate on cyanuric acid. It is very stable and cannot be converted into the iso-compound. L. T. T.

Chlorinated Methyl Isocyanurate and the Constitution of Cyanuric Acids. By A. W. Hofmann (*Ber.*, **19**, 2084—2098).—The author after carefully discussing the evidence of the constitution of cyanuric acid and melamine, still maintains that the balance of evidence is in favour of these compounds being normal derivatives, and their formulæ $[N : C{\cdot}OH]_3$ and $[N : C{\cdot}NH_2]_3$, and not iso-compounds of the formulæ $(CO : NH)_3$ and $[NH : C : NH]_3$ respectively.

Trichlorotrimethyl isocyanurate, briefly described in a previous paper (this vol. p., 43), has been further investigated. It crystallises in hexagonal scales which melt at 184°; it is easily soluble in ether, glacial acetic acid, chloroform, benzene, and nitrobenzene, sparingly in water and light petroleum. It boils without decomposition at a temperature far above 300°, and the distillate solidifies to a white brittle mass resembling meta-styrene. Attempts to replace the chlorine-atoms were unavailing, the methyl-group being always split off. When heated with water at 100°, it yields normal cyanuric acid, hydrochloric acid, and aldehyde. Heated with ammonia at 100°, it is decomposed into cyanuric acid and hexamethylenetetramine hydrochloride. When oxidised with permanganate or nitric acid, it gives dimethylisocyanuric acid.

Ponomareff has lately stated (this vol., p. 217) that, when ethyl or

methyl iodide is allowed to act on silver cyanurate at ordinary temperatures, although the principal product is ethyl or methyl isocyanurate, a small quantity of the normal cyanurate is also formed. The author has repeated this experiment with methyl iodide, but was not successful in obtaining the normal salt.

In the conversion of the dialkylcyanuric acids by heat into dialkylisocyanuric acids, it is possible that only the alkyl radicles have migrated to the iso-positions. In the hope of deciding between the two possible formulæ, $<_{-\,CO\cdot NMe\cdot CO\,-}^{NMe\cdot C(OH):N}>$ and $<_{CO\cdot NMe\cdot CO}^{NMe\cdot CO\cdot NH}>$, the author left methyl and ethyl iodides in contact with silver dimethylisocyanurate at the ordinary temperature for a long time. With methyl iodide, trimethyl isocyanurate only was obtained, and the mother-liquors when heated with hydrochloric acid in closed tubes gave no evolution of methyl chloride. With ethyl iodide, also, only triethyl isocyanurate could be isolated, but when the mother-liquors were heated with hydrochloric acid, methyl chloride was evolved. This would seem to point to the presence in these mother-liquors of an asymmetric triethyl cyanurate, having one ethyl radicle in the form of an ethoxy-group, and to the probability of the first of the above formulæ being the correct one for the dialkylcyanuric acids described (see preceding Abstract) by the author. In this case, the non-formation of such an asymmetrical methyl-derivative is probably due to the facility with which the normal methyl-derivatives pass into the iso-compounds. L. T. T.

The Inversion of Cane-sugar by Benzoic Acid and the Hydroxybenzoic Acids. M. Koral (*J. pr. Chem.* [2], **34**, 109—112).—Ostwald has shown by his electrical method that parahydroxybenzoic is a weaker acid than benzoic acid, although it contains an additional hydroxyl-group. The inversion constants have been determined at 25°, and found to be for benzoic acid 0·02264, for salicylic acid 0·1176, for metahydroxybenzoic acid 0·0292, and for parahydroxybenzoic acid 0·0114. The relative strengths of the acids have been determined at 45°: viz., benzoic 1·0, salicylic 5·505, metahydroxybenzoic 1·294, parahydroxybenzoic 0·532. These figures confirm Ostwald's results. There are several arithmetical errors in the paper. H. B.

Formation of Methane and Carbonic Anhydride from Cellulose. By F. Hoppe-Seyler (*Zeit. physiol. Chem.*, **10**, 401—440).—If the gases evolved from the mud of sewers, marshes, &c., contained in flasks are collected over mercury, they are found to consist after a time of almost equal volumes of carbonic anhydride and marsh-gas. If sea-water be added to the mud there is the same phenomenon, but the water of the Dead Sea prevented any evolution of gas. This gas undoubtedly comes from the cellulose in the vegetable remains in the muds. Van Tieghem (*Compt. rend.*, **88**, 205, **89**, 5) describes certain fungi (amylobacterium) as being concerned in the decomposition of cellulose. In the present research, sterilised filter-paper was used as a source of cellulose. In distilled

water it undergoes no change; in the presence of a small quantity of mud, the above-mentioned gases are formed abundantly if these amylobacteria are present; and no gas is found if they are absent. In a prolonged research lasting three and a half years, the gases were carefully collected, and analysed; the residue was then examined and analysed; the initial condition of the contents of the flask being known, it is found that carbonic anhydride and methane are the sole products of decomposition of cellulose by this ferment; thus differing from all known fermentation processes among carbohydrates. The cellulose first takes up a molecule of water, forming a non-reducing sugar ($C_6H_{12}O_6$), which then splits into $3CO_2 + 3CH_4$. Such experiments must be performed in the dark to avoid the error which in sunlight would arise from the presence of chlorophyll in the algæ of the mud. The chlorophyll is not destroyed even after being four years in the dark. Caoutchouc stoppers must not be used, as the author finds that diffusion of the gases takes place through such stoppers. W. D. H.

Analogues of Choline. By L. Niemilowicz (*Monatsh. f. Chem.*, **7**, 241—255).—By the action of trimethylamine on monochloracetone, the chloride of a base, $COMe{\cdot}CH_2{\cdot}NMe_3Cl$, is produced; it is proposed to call this substance *coprine chloride*. In its formation and composition it may be considered as analogous to choline and betaïne; coprine chloride is obtained as a crystalline very deliquescent mass, and is very stable in methyl and ethyl alcohols. Its aqueous solution gives all the reactions of the alkaloïds. Its *platinochloride* crystallises in golden-red needles, probably belonging to the monoclinic system; its *aurochloride* in glistening prisms which melt at 139·5°, and are at the same time completely decomposed. In its physiological action, this base resembles but is not identical with curari.

In like manner trimethylamine reacts with dichlorhydrin to form the chlorides of two bases, called *sepine* $CH_2Cl{\cdot}CH(OH){\cdot}CH_2{\cdot}NMe_3Cl$, and *aposepine*, $NMe_3Cl{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NMe_3Cl$, best separated by fractional crystallisation of their platinochlorides, that of the former being the less soluble. *Sepine platinochloride* forms aggregates of small, pale-yellow crystalline scales, and the *aurochloride* fragile, crystalline tablets. *Aposepine platinochloride* crystallises in rosy-red tables; and the *aurochloride* forms a sulphur-yellow crystalline powder. From the double salts, the chlorides of the bases were obtained in deliquescent white crystals, solutions of which give all the characteristic reactions of the alkaloïds. V. H. V.

Isoglucosamine. By E. Fischer (*Ber.*, **19**, 1920—1924).—*Phenylglucosazone* (Abstr., 1884, 53) is prepared by heating 100 grams of cane-sugar dissolved in 1 litre of water with 10 grams of strong sulphuric acid for one hour at 100°; 100 grams of phenylhydrazine and 170 grams of sodium acetate are added, and the whole warmed for 1½ hours on a water-bath. It is then filtered and washed successively with water and alcohol.

Isoglucosamine, $C_6H_{13}NO_5$, is obtained by treating finely powdered phenylglucosazone suspended in 6 parts of alcohol and 2 parts of

water at 40—50° with 2½ parts of zinc-dust and 1 part glacial acetic acid. It is kept at a temperature of 50°, and vigorously shaken until the glucosazone is entirely dissolved. It is then filtered, freed from zinc by means of hydrogen sulphide, and evaporated to a syrup under diminished pressure at 50°. The product, when treated with much absolute alcohol, yields a dark syrup which deposits crystals of *isoglucosamine acetate* after a time. On adding alcohol to the aqueous solution of this acetate, it separates in groups of slender needles. When heated it becomes brown at 135° and then melts slowly. The *hydrochloride* and sulphate form syrups. The *picrate* forms groups of slender, yellow crystals; the *oxalate* is crystalline and decomposes at 140—145° with evolution of gas; it dissolves very readily in water but is almost insoluble in alcohol. The free base forms a syrup soluble in alcohol, having most of the properties of its isomeride. The aqueous solutions of its salts are strongly lævorotatory. The relation of the base to lævulose therefore appears to be the same as that of glucosamine to dextrose. N. H. M.

Tetramethylenedicarboxylic Acid (1, 2). By W. H. Perkin, Jun. (*Ber.*, **19**, 2038—2044).—In the preparation of trimethylenedicarboxylic acid by the action of ethylene bromide on ethyl sodiomalonate, a small quantity of oil of a high boiling point is formed. This is found to be *ethyl butanetetracarboxylate*, $C_4H_6(COOEt)_4$, formed according to the equation $2CHNa(COOEt)_2 + C_2H_4Br_2 = C_4H_6(COOEt)_4 + 2NaBr$. This ethyl salt boils at 275—280° under 225 mm. pressure; it is a thick, colourless oil, which is still liquid at 0°; the yield is small. On hydrolysis, it yields *butanetetracarboxylic acid*, $C_4H_6(COOH)_4$, which, when heated, is decomposed into carbonic anhydride and adipic acid.

When ethyl butanetetracarboxylate is treated with sodium ethoxide, the disodio-compound, $C_2H_4[CNa(COOEt)_2]_2$, is formed, and this by the action of bromine may be converted into *ethyl tetramethylenetetracarboxylate* (1, 1, 2, 2), $C_4H_4(COOEt)_4$. The ethyl salt on hydrolysis yields *tetramethylenetetracarboxylic acid* (1, 1, 2, 2), which may be obtained in colourless crystals. The acid melts at 145—150°, and at a slightly higher temperature carbonic anhydride is evolved and *tetramethylenedicarboxylic acid* (1, 2), $\begin{matrix} CH_2\cdot CH\cdot COOH \\ | \quad\quad | \\ CH_2\cdot CH\cdot COOH \end{matrix}$, is formed. As considerable quantities of bye-products are also produced, it is better to heat an aqueous solution of the tetracarboxylic acid in closed tubes at 180—200°. The acid prepared in this way forms a syrupy mass. It could not be obtained in a crystalline form, and was therefore converted into the *ethyl salt*, a colourless liquid boiling at 238—242°. The acid may be obtained by hydrolysis of the purified ether in colourless feathery crystals melting at 130°; it forms characteristic salts. On oxidation with alkaline permanganate, oxalic acid is produced. When the acid is heated at 300°, water is given off and *tetramethylenedicarboxylic anhydride* is formed; this is crystalline and melts at 76—78°. It is sparingly soluble in ether and benzene, easily in alcohol. Heated with resorcinol at 250°, it yields a red melt, which shows the

fluoresceïn reaction. The formation of this anhydride proves that the two carboxylic groups are united to neighbouring carbon-atoms.

L. T. T.

Solubilities of the Acids of the Oxalic Series and of their Salts. By Z. N. Miczyński (*Monatsh. Chem.*, **7**, 255—272).—In this paper, a number of determinations are given of the solubility of some acids of the oxalic series and of their salts, and empirical formulæ are deduced from the results. The heating and cooling methods were both used. The principal results are given below:—

Oxalic acid, $S = 3{\cdot}543 + 0{\cdot}1759\ (t - 0{\cdot}5) + 0{\cdot}002721\ (t - 0{\cdot}5)^2 + 0{\cdot}0000104\ (t - 0{\cdot}5)^3$.

Calcium malonate, $S = 0{\cdot}2897 + 0{\cdot}00423t - 0{\cdot}0000233t^2$.

Barium malonate, $S = 0{\cdot}1438 + 0{\cdot}00382\ (t - 0{\cdot}2) - 0{\cdot}0000192\ (t - 0{\cdot}2)^2$.

Succinic acid, $S = 2{\cdot}883 + 0{\cdot}1583\ (t - 0{\cdot}5) + 0{\cdot}000372\ (t - 0{\cdot}5)^2 + 0{\cdot}000105\ (t - 0{\cdot}5)^3$.

Calcium succinate, from 24—41°, $S = 1{\cdot}291 + 0{\cdot}01114\ (t - 0{\cdot}2) + 0{\cdot}00001894\ (t - 0{\cdot}2)^2$; from 41°, $S = 1{\cdot}152 - 0{\cdot}0152\ (t - 41{\cdot}6) + 0000581\ (t - 41{\cdot}6)^2$.

Barium succinate, from 0—12°, $S = 0{\cdot}421 + 0{\cdot}000745 + 0{\cdot}000031t^2$; from 24°, $S = 0{\cdot}4077 - 0{\cdot}00248\ (t - 24{\cdot}3) - 0{\cdot}0000102\ (t - 24{\cdot}3)^2$.

Calcium isosuccinate, $S = 0{\cdot}5216 + 0{\cdot}0000705\ (t - 0{\cdot}2) - 0{\cdot}000047\ (t - 0{\cdot}2)^2$.

Barium isosuccinate, $S = 1{\cdot}905 + 0{\cdot}1065\ (t - 0{\cdot}2) - 0{\cdot}00101\ (t - 0{\cdot}2)^2$.

The results calculated from the above formulæ are in fair accordance with those observed.

V. H. V.

A Peculiar Reaction of Malonic Acid. By S. Kleemann (*Ber.*, **19**, 2030—2032).—Malonic acid dissolves readily in cold acetic anhydride, but on heating the solution, carbonic anhydride is evolved, and the liquid becomes of a yellowish-red colour with a strong yellowish-green fluorescence; the latter is especially marked on adding glacial acetic acid. The reaction is very sensitive, being produced with a milligram of malonic acid. Metallic malonates show the reaction slightly, but the ethyl salt does not do so at all.

In preparing the new compound, it is best to heat a mixture of 1 part of malonic acid, 1 part of anhydrous sodium acetate, and 3 parts of acetic anhydride gently on a water-bath. The yield is small, much of the malonic acid being decomposed into acetic acid and carbonic anhydride. The sodium compound, $C_{11}H_3O_8Na$, forms a brownish-yellow powder. Hydrochloric acid precipitates the free acid from its aqueous solution in pale yellow flocks having the composition $C_{11}H_4O_8$.

A solution in dilute acetic acid evolves carbonic anhydride, and the remaining liquid appears to contain resinous matter only. When the sodium compound in acetic solution is boiled with phenylhydrazine, carbonic anhydride is evolved, and an orange-yellow compound of the formula $C_{22}H_{16}N_4O_4$ is formed. The reaction appears to take place according to the equation $C_{11}H_3O_8Na + 2NHPh{\cdot}NH_2 + C_2H_4O_2 =$

$C_{10}H_4O_4(N{\cdot}NHPh)_2 + CO_2 + 2H_2O + NaC_2H_3O_2$. This hydrazine is soluble in alcohol, glacial acetic acid, alkalis, and strong hydrochloric acid; insoluble in water and ether. Strong sulphuric acid dissolves it, yielding a green solution, from which it is again precipitated on the addition of water. It melts with decomposition at 180°.

L. T. T.

Normal Pentahydroxypimelic Acid and its Lactone. By H. Kiliani (*Ber.*, **19**, 1916—1920).—The *lactone* of pentahydroxypimelic acid, $C_7H_{10}O_8$, is obtained by digesting the lactone of dextrose-carboxylic acid with an equal weight of nitric acid (sp. gr. 1·2) at 40° for 24 hours. The product is diluted with hot water (500 grams of water to 10 grams of lactone), boiled for 15 minutes with an excess of calcium carbonate and filtered hot. The calcium salt is digested with the equivalent amount of oxalic acid, filtered, and evaporated. The red syrup thus obtained is mixed with an equal volume of absolute alcohol, and kept over sulphuric acid, when the lactone separates in short slender needles. It melts at 143°, dissolves very readily in water, more sparingly in alcohol, and is soluble in ether.

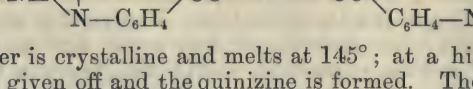
Hydrogen potassium pentahydroxypimelate was prepared, and also the *barium* (with 3 mols. H_2O), and *calcium* (with 4 mols. H_2O) *salts*.

N. H. M.

α-δ-Diacetadipic Acid. By W. H. Perkin, Jun., and M. Obrembsky (*Ber.*, **19**, 2045—2055).—From the high boiling residue obtained in the preparation of ethyl acetotrimethylenecarboxylate by the action of ethylene bromide on ethyl sodacetoacetate (Perkin, Trans., 1885, 829), the authors have isolated *ethyl diacetadipate*, $COOEt{\cdot}CHAc{\cdot}CH_2{\cdot}CH_2{\cdot}CHAc{\cdot}COOEt$. This ethyl salt, purified by distillation in a current of steam and conversion into the sodium compound, was reconverted into the ether by dilute sulphuric acid; it is a thick, colourless oil, and gives a dark reddish-violet coloration with ferric chloride. The *disodium-derivative* is pale-yellow and amorphous. With phenylhydrazine, the ethyl compound yields *ethyl diphenylizindiacetadipate*,

$$<^{NPh}_{NH}>CMe{\cdot}CH(COOEt){\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOEt){\cdot}CMe<^{NPh}_{NH}>,$$

together with *ethylene-dimethyloxyquinizine*,



The former is crystalline and melts at 145°; at a higher temperature alcohol is given off and the quinizine is formed. The latter is soluble in alkalis and acids, but insoluble in neutral solvents; it is still solid at 250°. These compounds resemble those obtained from ethyl diacetosuccinate by Knorr and Bülow (Abstr., 1884, 1381). Ethyl diacetadipate dissolves in concentrated alcoholic ammonia, and the solution, after a time, deposits crystalline scales having the composition $C_{14}H_{24}N_2O_4$. These melt at 177°, and are probably *ethyl diamidodiethylideneadipate*,

$$NH_2{\cdot}CMe : C(COOEt){\cdot}CH_2{\cdot}CH_2{\cdot}C(COOEt) : CMe{\cdot}NH_2$$

it forms a platinochloride. When heated at 100°, ammonia is evolved, but the authors have not yet been able to determine whether the expected imide is formed. When ethyl diacetadipate is distilled in a vacuum, water is eliminated, and an oil formed which boils at 320—231° under 225 mm. pressure. It has the composition $C_{14}H_{20}O_5$, and its constitution is probably $COOEt{\cdot}CH<\begin{matrix}CO{\cdot}CH:CMe\\ CH_2\text{——}CH_2\end{matrix}>CH{\cdot}COOEt$. An alcoholic solution gives an intense violet coloration with ferric chloride. This compound is also produced, in a pure state, when ethyl diacetadipate is dissolved in concentrated sulphuric acid; it forms an unstable sodium-derivative. When heated with alcoholic potash, it yields *methylketodehydroheptamethylenedicarboxylic acid*, $COOH{\cdot}CH<\begin{matrix}CO{\cdot}CH:CMe\\ CH_2\text{——}CH_2\end{matrix}>CH{\cdot}COOH$, together with *methylketodehydroheptamethylene*, $CH_2<\begin{matrix}CO{\cdot}CH:CMe\\ CH_2\text{——}CH_2\end{matrix}>CH_2$. The acid crystallises in flat plates melting at 189°. At 250°, carbonic anhydride is evolved, and a new acid formed, the constitution of which has not yet been determined. The second compound forms a colourless neutral oil boiling at 188—190°, and having an odour resembling that of camphor. It forms oily compounds with phenylhydrazine. The ethyl-derivative when treated with phosphoric chloride yields a *dichloro-derivative*, $C_{14}H_{20}O_4Cl_2$; this is a colourless unstable oil, which gradually evolves hydrochloric acid. When boiled with zinc-dust, it yields the *monochloro-derivative*, $C_{14}H_{19}ClO_4$; this is a colourless oil boiling at 170—175° under 50 mm. pressure, and smelling like turpentine.

When ethyl disododiacetadipate is treated with iodine, it yields *ethyl diacetyltetramethylenedicarboxylate*, a pale coloured oil, which, on hydrolysis, yields the free acid, crystallising in micaceous flakes with 2 mols. H_2O. This acid loses its water in a vacuum or at 80°, and melts at 210° with evolution of carbonic anhydride and formation of a high boiling oil. The acid is easily soluble in alcohol, ethyl acetate, and boiling water, sparingly in benzene and chloroform.

L. T. T.

Compounds of Aldehydes, Ketones, and Ketonic Acids, with Thioglycolic and Thiacetic Acids. By J. Bongartz (*Ber.*, **19**, 1931—1935).—When anhydrous thioglycollic acid is mixed with aldehydes, a reaction in most cases takes place, with development of heat; in other cases, the reaction takes place only in presence of hydrogen chloride or zinc chloride.

Dithiobenzaldehydeacetic acid, $CHPh(S{\cdot}CH_2{\cdot}COOH)_2$, crystallises from its aqueous solution in needles, melting at 123—124°. *Dithiocinnamaldehydeacetic acid* forms colourless plates, which melt at 145—146°. *Dithiorthohydroxybenzaldehydeacetic acid* melts at 151—152°. *Dithiometanitrobenzaldehydeacetic acid* forms colourless crystals, melting at 134—135°; the *para-compound* crystallises in lustrous, yellowish plates, which melt at 164—165°.

Thioglycollic acid reacts with ketones only in presence of zinc chloride or hydrogen chloride.

Dithiacetoneacetic acid, $CMe_2(S{\cdot}CH_2{\cdot}COOH)_2$, crystallises from chloroform in clear crystals, melting at 133—135°. *Dithiacetophenoneacetic acid*, $CMePh(S{\cdot}CH_2{\cdot}COOH)_2$, crystallises from ether in large needles, which melt at 138—139°. *Dithiobenzophenoneacetic acid* is formed when its constituents are heated with zinc chloride at 100°. It melts at 163—164°.

Thiopyruvacetic acid, $COOH{\cdot}CMe(OH){\cdot}S{\cdot}CH_2{\cdot}COOH$, is prepared by mixing pyruvic and thioglycollic acids; the reaction is accompanied with rise of temperature. It forms colourless crystals, melting at 109—110°. It is decomposed by water into its constituents. When the melted substance is treated with hydrogen chloride, it is converted into *dithiopyruvacetic acid*, $COOH{\cdot}CMe(S{\cdot}CH_2{\cdot}COOH)_2$. The latter dissolves readily in water, and melts at 159—160°.

Dithioacetylbenzaldehyde, $CHPh{\cdot}(S{\cdot}COMe)_2$, is obtained by passing dry hydrogen chloride through a mixture of benzaldehyde and thiacetic acid. It crystallises in slender needles, and melts at 147—148°.

When the dithioaldehydeacetic acids, $CHR(S{\cdot}CH_2{\cdot}COOH)_2$, are treated with dilute potassium permanganate solution, disulphones are formed. The *disulphone of benzylidene*, $CHPh(SO_2Me)_2$, crystallises from water in slender needles, melting at 162—163°; the *dimethylsulphone of metanitrobenzylidene*, $NO_2{\cdot}C_6H_4{\cdot}CH(SO_2Me)_2$, melts at 181—182°; the *para-compound* melts at 239—240°. N. H. M.

Some Disubstituted Derivatives of Pyrroline and their Constitution. By G. Ciamician and P. Silber (*Ber.*, **19**, 1956—1964).—*Pyrrolketonedicarboxylic acid*, $COOH{\cdot}C_4NH_3{\cdot}CO{\cdot}COOH$, is obtained by mixing a warm solution of 5 grams of pyrrylene-dimethyldiketone in 500 c.c. of water containing potash, with a boiling solution of 28 grams of potassium permanganate in 730 c.c. of water. It is afterwards filtered, and the precipitate extracted several times with boiling water. The filtrate is evaporated down, treated with dilute sulphuric acid and quickly extracted 10 or 12 times with ether. The acid is crystalline, and readily soluble in ether, alcohol, and acetone, almost insoluble in benzene, chloroform, &c. The *silver salt* forms a canary-coloured precipitate. The *dimethyl compound*, $C_7H_3NO_5Me_2$, crystallises from boiling water in long needles, melting at 144—145°. When the potassium salt is fused with potash, it is converted into *potassium pyrryldicarboxylate*, $C_4NH_3(COOK)_2$.

The *free acid* is soluble in ether, acetone, hot water, and alcohol, insoluble in ethyl acetate, benzene, &c. It decomposes at 260°, with evolution of carbonic anhydride. The silver salt forms a white curdy precipitate; the *barium salt* crystallises from water in lustrous needles. The *dimethyl salt* separates from its aqueous solution in long needles, melting at 132°. It is readily soluble in ether, alcohol, and benzene. The *diethyl salt* melts at 82°.

Pyrrylketonedicarboxylic acid is also formed when pyrrylmethylketonecarboxylic acid is oxidised with potassium permanganate. The two acetyl-groups in pyrrylenedimethylketone must therefore have the same position as the acetyl and carboxyl groups in pyrrylmethylketonecarboxylic acid.

When potassium pyrrylmethylketonecarboxylate is heated with potassium carbonate at 280—300° in a retort, an oil distils over which soon solidifies. It is pyrryl methyl ketone, and melts at 90—91°. The formation of this ketone, together with the fact that methylic pyrrylmethylketonecarboxylate can be obtained directly from methylic pyrrylcarboxylate, show that the two substituted radicles replace symmetrical hydrogen-atoms; the constitution represented by the general formula $<\begin{matrix}CH\cdot CR\\CH\cdot CR\end{matrix}>NH$, in which the substitution has taken place in the CH-group, adjacent to the imide-group, is the most probable (compare this vol., p. 626). N. H. M.

Presence of Ordinary Cymene and an Aromatic Hydrocarbon, C_9H_{12}, in Resin Spirit. By W. Kelbe (*Ber.*, **19**, 1969—1970).—Paracymene was found to be present in the mother-liquor obtained in the separation of metisocymene from resin spirit. The sulphonamide melts at 115·5° (not at 111—112°, as given by Jacobsen).

In sulphonating the fraction of resin spirit boiling below 160°, a *barium salt*, $(C_9H_{11}SO_3)_2Ba + H_2O$, was obtained. The *sulphonamide* crystallises from water in plates, melting at 130°. N. H. M.

Nitrophenyl Benzoates and Nitrobenzoates and their Products of Decomposition. By G. Neumann (*Ber.*, **19**, 2018—2022).—Continuing his previous work (this vol., p. 350), the author slowly dissolved orthonitrophenyl benzoate in a mixture of equal parts of nitric acid of sp. gr. 1·52, and sulphuric acid of sp. gr. 1·82. A trinitrated nitrobenzoate was not obtained, but the products of the reaction contained trinitrophenol and metanitrobenzoic acid. Trinitrophenyl nitrobenzoate was probably first formed, and then decomposed by the sulphuric acid.

Paranitrophenol, when heated with benzoic chloride, yields *paranitrophenyl benzoate*. The reaction is at first very violent, and great care must be taken to avoid an explosion. The salt crystallises in thin colourless and efflorescent needles, melting at 142·5°. It is soluble in chloroform, alcohol, ether, benzene, &c. When dissolved in nitric acid of sp. gr. 1·48, it yields *paranitrophenyl metanitrobenzoate*. This is easily soluble in boiling alcohol and glacial acetic acid, crystallises in soft, silky, colourless needles, and melts at 135·5°. When this compound is dissolved in nitric acid of sp. gr. 1·53, it yields orthoparadinitrophenyl metanitrobenzoate, already obtained from orthonitrophenyl benzoate. With a mixture of nitric and sulphuric acids, the reaction was the same as in the case of the ortho-compound, trinitrophenol and benzoic acid being produced. L. T. T.

Method for Preparing Primary Amines. By J. Tafel (*Ber.*, **19**, 1924—1931).—Ethylamine can be prepared by heating a cooled solution of 1 part of ethylidenephenylhydrazine in 5 parts of 96 per cent. alcohol, with small quantities of 2 per cent. sodium amalgam and glacial acetic acid, the latter being always in excess. It is then supersaturated with concentrated soda solution and distilled. The distillate is made acid with sulphuric acid, evaporated, and the syrup obtained

is mixed with much powdered caustic potash; ethylamine is given off, with great development of heat, and may be condensed by the use of a freezing mixture. The yield is 45 per cent. of the theoretical. In a similar manner, isopropylamine was prepared from acetonephenylhydrazine. The yield was 70 per cent. of the theoretical.

Pentylamine, $CH_2Me{\cdot}CH_2{\cdot}CHMe{\cdot}NH_2$, is obtained by treating 1 part of methylpropylketone-phenylhydrazine dissolved in 10 parts of alcohol with 25 parts of 2·5 per cent. sodium amalgam, and the necessary amount of glacial acetic acid. It boils at 89—91°, under 755 mm. pressure. It is a mobile oil, having a strong ammoniacal odour, and is miscible in all proportions with water, ether and alcohol. The *hydrochloride* forms lustrous needles; the *normal oxalate* crystallises from alcohol in plates; *hydrogen pentylamine oxalate* and the *platinochloride* were also prepared.

Phenylethylamine, $CHMePh{\cdot}NH_2$, is prepared by heating 12 grams of phenylhydrazine-acetophenone dissolved in 50 grams of alcohol with 325 grams of 2·5 per cent. sodium amalgam and glacial acetic acid. It forms an oil, boiling at 182—185° under 741 mm. pressure; rather readily soluble in water, miscible in alcohol and ether. The *hydrochloride* crystallises in groups of needles, readily soluble in alcohol and ether. It melts at 155°. The *sulphate* forms stellate groups of plates, very readily soluble in water. It melts at 170°. The *oxalate* and *platinochloride* are also described.

Phenylpropylamine, $C_9H_{13}N$, is prepared from cinnamaldehydephenylhydrazine. It is purified by means of the oxalate. It boils at 215—216° (uncorr.) under 752 mm. pressure, is not very readily soluble in water, but is miscible with alcohol and ether. It absorbs carbonic anhydride from the air very readily, with formation of a white, crystalline mass.

Œnanthylamine (b. p. 153—154° under 741 mm. pressure) and benzylamine were prepared in a manner similar to the above compounds. N. H. M.

Removal of Methyl from Tertiary Aromatic Amines. By W. Staedel (*Ber.*, **19**, 1947—1949).—When pure dimethylaniline (2 parts) is treated with acetic bromide (1 part), trimethylphenylammonium bromide and methylacetanilide are formed.

Methylacetometachloranilide, $C_6H_4Cl{\cdot}NMeAc$, may be prepared from dimethylmetachloraniline (2 mols.) and acetic bromide (1 mol.). The product is extracted first with water, which dissolves the trimethylmetachlorophenylammonium bromide formed in the reaction, and then with ether. It crystallises from benzene in plates, which melt at 92·5, and boil above 245°.

Ethylacetanilide was prepared from diethylaniline in a similar manner. N. H. M.

Introduction of Methyl into Metanitraniline. By W. Staedel and H. Bauer (*Ber.*, **19**, 1939 — 1946).—Reinhardt and Staedel previously (Abstr., 1883, 578) showed that the substitution of methyl and ethyl in aromatic amines will take place at a much

lower temperature if the hydrobromides of the bases are used instead of the hydrochlorides.

Nitraniline hydrobromide, $NO_2 \cdot C_6H_4 \cdot NH_2,HBr$, is prepared by quickly adding finely-divided nitraniline to cold 45 per cent. hydrobromic acid solution; the whole solidifies to a mass of lustrous plates. It is readily soluble in water.

Trimethylmetanitrophenylammonium bromide, $NO_2 \cdot C_6H_4 \cdot NMe_3Br$, is obtained, together with metanitrodimethylaniline, when metanitraniline is heated for 8 to 10 hours on a water-wath with rather more than 3 mols. of methyl alcohol. It dissolves readily in water and separates in well-formed colourless prisms. Freshly precipitated silver chloride converts it into the *chloride;* the latter resembles the bromide.

Trimethylmetanitrophenylammonium hydroxide, obtained by the action of silver or lead oxide on the bromide, is very unstable; it absorbs carbonic anhydride quickly from the air. On evaporating its solution, even at a low temperature, it decomposes with formation of nitrodimethylaniline. The *carbonate* of the ammonium base is also unstable. In preparing the ammonium hydroxide from the bromide, small quantities of metanitrophenol and trimethylamine are formed.

Metanitrodimethylaniline is readily obtained by heating an aqueous solution of the hydroxide of the quaternary base at 150°. It forms large monoclinic prisms, $\breve{a} : \bar{b} : \dot{c} = 0{\cdot}9123 : 1 : 0{\cdot}6758$, soluble in ether and benzene. It melts at 59—60°.

Metamidodimethylaniline is a liquid boiling at 258°. The *hydrochloride* crystallises in prisms. The *acetyl-derivative* separates from its solution in dilute alcohol in needles melting at 87°.

Trimethylmetanitrophenylmetanitrophenoxide,

$$NO_2 \cdot C_6H_4 \cdot NMe_3 \cdot O \cdot C_6H_4 \cdot NO_2 + 3H_2O,$$

is obtained by mixing the free ammonium base with metanitrophenol. It forms large, orange-red plates, readily soluble in water; it melts at 62°. N. H. M.

Action of Concentrated Hydrochloric Acid on Nitrosodimethylaniline. By R. Möhlau (*Ber.*, **19**, 2010—2013).—200 grams of nitrosodimethylaniline hydrochloride are warmed with 1 kilo. of hydrochloric acid at 100—105°, and allowed to cool. After 24 hours, crystals of *dichloroparaphenylenediamine hydrochloride* separate. The *free base*, $C_6H_2(NH_2)_2Cl_2$ [= 1 : 4 : 2 : 5], crystallises from water in lustrous prisms, melting at 164°. When oxidised, it yields paradichloroquinone. *Dichloroquinonedichlorimide*, $C_6H_2Cl_2<\begin{matrix}NCl\\NCl\end{matrix}>$, is obtained by the action of chloride of lime on a solution of the base in hydrochloric acid. It forms prisms melting at 134—135°.

The mother-liquor from the nitrosodimethylaniline hydrochloride was found to contain dimethylparaphenylenediamine and dimethyldiparachloroparaphenylenediamine. N. H. M.

Action of Orthotoluidine on Quinol and Resorcinol. By M. Philip (*J. pr. Chem.* [2], **34**, 57—73).—*Parahydroxyphenylorthotolylamine*, $HO \cdot C_6H_4 \cdot NH \cdot C_6H_4Me$, quinol, orthotoluidine, and calcium

chloride are heated together at 240—250°, the product fractionated in a current of hydrogen, and that portion boiling below 370° crystallised from mixed benzene and light petroleum. It melts at 90°, and boils at 382—384° (corr.) in hydrogen without decomposition. It is almost insoluble in water, but its solution in alkalis decomposes quickly. When heated with concentrated hydrochloric acid at 240°, it is decomposed into quinol and orthotoluidine. Heated with zinc-dust, it gives hydroacridine and acridine, the intermediate phenyl-orthotolylamine not being formed. Dry hydrogen chloride passed into the ethereal solution causes the separation of the crystalline *hydrochloride*, $C_{13}H_{13}NO,HCl$; it is decomposed by moist air. The *dimethyl-*, *formyl-*, *diacetyl-*, and *dibenzyl-derivatives* were prepared by heating with methyl iodide, formic acid and sodium formate, acetic acid and sodium acetate, and benzoic chloride respectively; the first boils at 335—336°, and is a liquid; the other three are crystalline, and melt at 136·5°, 106°, and 171° respectively.

Diorthotolylparaphenylenediamine, $C_6H_4(NH\cdot C_7H_7)_2$.—This is always produced in the preparation of the preceding compound, and by employing a higher temperature (280—290°) and less quinol, it may be obtained in large quantity. It is colourless, crystalline, melts at 135°, boils at 420°, and is scarcely dissolved by dilute acids. The crystalline *hydrochloride*, $C_{20}H_{20}N_2,2HCl$, is instantly decomposed by water. The *dimethyl-*, *diformyl-*, *diacetyl-*, *dibenzoyl-*, and *dinitroso-derivatives* are described; the first is a liquid boiling at 385—390°; the others are crystalline, and melt at 165°, 186°, 235°, and 140° respectively.

Metahydroxyphenylorthotolylamine, $HO\cdot C_6H_4\cdot NH\cdot C_7H_7$.—Resorcinol and orthotoluidine are heated at 260—280°, the product fractionated, and that portion which boils at 355—360° is converted into the formyl-derivative, then recrystallised, and decomposed by hydrochloric acid. It is a coloured oil boiling at 370—375°. It dissolves in warm dilute acids and in alkalis; the mono-formyl-derivative melts at 169°. Heated with zinc-dust, it also yields hydroacridine and acridine.

No phenylorthotolylparaphenylenediamine could be obtained by heating aniline with parahydroxyphenylorthotolylamine, but only diphenylparaphenylenediamine. H. B.

Influence of Substituted Elements and Radicles on the Shade of some Dyes. By K. Heumann and T. Heidlberg (*Ber.*, **19**, 1989—1993).—*Dichloropararosaniline*, $OH\cdot C(C_6H_3Cl\cdot NH_2)_2\cdot C_6H_4\cdot NH_2$, is obtained by heating 20·9 grams of paratoluidine, 50 grams of chlororthotoluidine, and 106 grams of 75 per cent. solution of arsenic acid for some hours at 190°. When cold, the product is boiled with water and filtered; the solution is treated with a small quantity of soda, filtered, and salted out. It is then dissolved in water, precipitated with ammonia, and extracted with ether to remove chrysaniline. It is soluble in alcohol, sparingly soluble in ether, and insoluble in water. With a small quantity of an acid, it yields a splendid bluish-red solution, whilst in presence of more acid the colour changes to a brownish-red. It dyes silk a magenta colour with a strong blue shade, whilst pararosaniline yields a yellowish-red.

When reduced, it yields a salt of the leuco-base; the free base forms a red crystalline mass, readily soluble in dilute acids. When para-toluidine (1 mol.) and metachloraniline (2 mols.) are heated with arsenic acid at about 190°, a base is formed, which dissolves in alcohol, yielding a reddish-yellow fluorescent solution. It is probably a chrysaniline.

Trichlorotriphenylrosaniline,

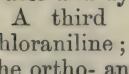
$$OH{\cdot}C(C_6H_4{\cdot}NH{\cdot}C_6H_4Cl)_2{\cdot}C_6H_3Me{\cdot}NH{\cdot}C_6H_4Cl,$$

is prepared by heating 10 grams of rosaniline, 100 grams of ortho-chloraniline, and 1·2 gram of benzoic acid for several hours at the boiling point of the chloraniline. On treating the product with hydrochloric acid, the dye is precipitated as a fine blue silt. This is filtered, dissolved in alcohol, and again precipitated with hydrochloric acid. The hydrochloride is a dark-blue powder, insoluble in water; the alcoholic solution has a splendid blue colour. The free *base* is obtained as a red flaky mass, on treating the alcoholic solution of the hydrochloride with ammonia; it is insoluble in water, but soluble in alcohol, ether, and benzene. When reduced with zinc-dust, the *leuco-base* separates as a white precipitate, which rapidly becomes blue on exposure to air. It dyes silk a blue-violet, corresponding with methyl-violet 3B.

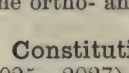
An *isomeric trichlorotriphenylrosaniline* was prepared from meta-chloraniline and rosaniline, in presence of benzoic acid. Its properties resemble those of the ortho-compound, but it dyes silk more strongly bluish-violet, corresponding with 6B. When treated with fuming sulphuric acid, a product was obtained which dissolved in water and dyed silk a pure blue.

A third *trichlorotriphenylrosaniline* was prepared from para-chloraniline; it dyed silk a bluish-violet of a shade between those of the ortho- and meta-compounds. N. H. M.

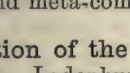
Constitution of the Aldehydines. By O. Hinsberg (*Ber.*, **19**, 2025—2027).—Ladenburg (Abstr., 1879, 233) ascribed the formula



, to this class of compounds in preference to either



or



When anhydrobenzoyldiamidotoluene (formed by melting together metaparatoluenediamine with benzoic acid) is heated in benzene solution with benzyl chloride at 160°, *monobenzylanhydrobenzoyl-diamidotoluene* is formed, together with a little of the dibenzyl-derivative. This compound the author finds to be identical with tolubenzaldehydine. It is thus clear that the latter is an anhydro-amidine, and it is probable that the aldehydines generally belong to this class of compounds; the third of the above formulæ, therefore, most correctly represents their constitution. L. T. T.

Azo-compounds. By W. Staedel and H. Bauer (*Ber.*, **19**, 1952—1956).—Diazoamidobenzene is conveniently prepared by gradually

adding a solution of sodium nitrite (18 parts) to aniline (50 parts), dissolved in 15 parts of sulphuric acid and 1500 parts of water. The temperature is kept at about 27° by the addition of ice. After 30 minutes, the whole is filtered, washed, and dried at the ordinary temperature. The yield is 97—98 per cent. of the theoretical.

To prepare amidoazobenzene, the above compound is dissolved whilst still moist in two to three times its weight of aniline; the solution is then mixed with an amount of aniline hydrochloride equal to one-tenth the weight of diazoamidobenzene, and kept for two hours at a temperature not above 40°. On adding the quantity of hydrochloric acid corresponding with the aniline present, the amidoazobenzene separates. The yield is almost quantitative.

Metanitrophenylazodimethylamidobenzene, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NMe_2$, is obtained by shaking together 10 grams of dimethyaniline, 11·3 grams of metanitraniline, 4—5 grams of sulphuric acid, and 600—700 c.c. of water, and as soon as the temperature has reached 27°, treating with 7 grams of sodium nitrite in 70 c.c. of water. In 30 minutes it is filtered, washed, and dried. It crystallises from alcohol, which dissolves it sparingly, in lustrous, red plates, melting at 159—160°. When treated with ammonium sulphide, it is decomposed, yielding metanitraniline and paramidomethylaniline. Zinc in presence of acid reduces it to metaphenylenediamine and paramidomethylaniline. This mixture, when oxidised, yields a splendid blue dye.

Metachlorophenylazodimethylamidobenzene, $C_6H_4Cl \cdot N_2 \cdot C_6H_4 \cdot NMe_2$, is prepared from metachloraniline and dimethylaniline in a manner similar to the above compound. It forms yellow plates, rather readily soluble in alcohol; it melts at 98°.

Metanitrophenylazometachlorodimethylamidobenzene,

$$NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4Cl \cdot NMe_2,$$

crystallises from alcohol in reddish-yellow plates, melting at 155—156°. When reduced with zinc and acid, it yields a mixture of bases; these on oxidation give a splendid blue dye.

N. H. M.

Synthesis and Constitution of the Two Propylbenzoic Acids, $C_3H_7 \cdot C_6H_5 \cdot COOH = [1:4]$. By R. Meyer (*J. pr. Chem.* [2], **34**, 91—104).—The details of the syntheses of primary propylbenzoic acid and of cumic acid (comp. Abstr., 1882, 840 and 971) are now recorded, in consequence of recent work by Widmann (*Ber.*, **19**, 245, &c.).

Cumic Acid.—(1.) Preparation from cumene derived from cumic acid, the latter being itself made from cumin oil. The cumene was converted into bromcumene, boiling at 216° (corr.), and the latter found to be pure. It was mixed with benzene, sodium added, and moist carbonic anhydride passed for 48 hours. The product was extracted with water, and the aqueous solution acidified, when cumic acid separated; the identity of this was established in all its properties except the melting point, which was 110° instead of 116—117°. All endeavours to raise the melting point by recrystallisation, &c., were unavailing, as also all attempts to convert the ordinary acid into a modification, melting at the lower temperature. (2.) Cumic

acid was therefore prepared from synthetical cumene. Isopropyl iodide prepared from glycerol was converted into the bromide by the direct action of bromine (comp. p. 929); the purified product, mixed with benzene, was gradually run on to aluminium bromide—prepared by the action of bromine on aluminium, and removal of excess of bromine by a stream of air—and the whole finally warmed. The cumene formed was separated by addition of water and fractional distillation, and was then treated with sodium and benzene as above; the cumic acid obtained melted at 116—117°.

Primary Propylbenzoic Acid.—Primary propylbenzene prepared by Fittig's method was brominated. *Parabromopropylbenzene* is a liquid boiling at 220° (corr.). When oxidised with nitric acid, it yields parabromobenzoic acid and a trace of another acid, probably orthobromobenzoic acid. Parabromopropylbenzene when treated with sodium and carbonic anhydride, as described above, yields parapropylbenzoic acid; this melts at 140°, and on oxidation with permanganate yields terephthalic acid and another substance not identified.

In neither of the above syntheses is the yield good, nor was a better one obtained by acting with sodium amalgam on parabromopropylbenzene and ethyl chlorocarbonate. In the last reaction, there is also formed *mercuric propylphenyl*, $Hg(C_6H_4 \cdot C_3H_7)_2$, a crystalline compound melting at 109—110°. H. B.

Preparation of Phenylacetic Acid. By W. Staedel (*Ber.*, **19**, 1949—1952).—100 grams of benzyl cyanide, boiling at 210—235° (prepared from the chloride by Mann's method) are added to 300 grams of dilute sulphuric acid (3 vols. acid to 2 vols. water), and the whole heated over a flame until a reaction begins; the flame is then removed, and in a few seconds the reaction becomes very violent. To avoid loss, the flask containing the substance is provided with a tube bent twice at right angles, the end of which is fitted into a double-necked flask containing water. A funnel is fitted into the second neck of the flask so that it dips under the water. To avoid water being ejected through the funnel, a dish is placed at the opening. When the first violence of the reaction ceases, the whole is heated for some time; the product is then mixed with water and washed to remove sulphuric acid. The best results are obtained when the reaction is very violent; care should therefore be taken that the mixture is sufficiently heated at first. The yield was 71·5 per cent. of the theoretical amount. N. H. M.

Isomerism in the Cinnamic Acid Series. By E. Erlenmeyer (*Ber.*, **19**, 1936—1938).—Erlenmeyer and Stockmeyer previously obtained (Stockmeyer, *Diss. Nuremberg*, 1883) an acid isomeric with bromocinnamic acid, melting at 153·5°, which when treated with sodium carbonate yielded phenylacetylene, β-bromostyrolene and phenylpropiolic acid. Concentrated sulphuric acid converts it into benzoylacetic acid and bromacetophenone. When a solution of the acid in glacial acetic acid at 0° is saturated with hydrogen bromide, an isomeride is obtained which melts at 159—160°. This, when heated with hydrobromic acid gives acetophenone and phenylethylaldehyde.

The author ascribes to the acids melting at 153·5° and 159—160° the respective formulæ $CPhBr:CH\cdot C(OH)<^{O}_{O}>C(OH)\cdot CH:CPhBr$ and $CPhBr:CH\cdot C(OH)<^{O}_{O}>C(OH)\cdot CBr:CPhH$ (comp. Michael and Browne, this vol., p. 702, and Michael, this vol., p. 687).

It is suggested that some cases of isomerism of carboxylic acids, and the formation of acid salts of monobasic carboxylic acids may be due to polymerisation (*Ber.*, **3**, 342). Thus tartaric acid would be a combination of dextro- and lævo-tartaric acids,

$$COOH\cdot CH(OH)\cdot CH(OH)\cdot C(OH)<^{O}_{O}>C(OH)\cdot CH(OH)\cdot CH(OH)\cdot COOH,$$

and fumaric acid, a combination of 2 mols. of maleic acid.

N. H. M.

Phenol Urea. By H. Eckenroth (*Arch. Pharm.* [3], 623—625).—This new compound is easily obtained perfectly pure from phenyl carbonate which has been recrystallised from alcohol; this is dissolved in a little boiling alcohol, the calculated amount of ammonia gradually added, and after digesting the mixture on the water-bath until the odour of ammonia has disappeared, allowing it to cool. The compound in question then crystallises out in small, colourless, lustrous plates. Phenol urea shows all the reactions of phenol and of urea; it is easily soluble in water and alcohol; the aqueous solution gives the well-known violet coloration with ferric chloride. Exposed to the air, the crystals readily effloresce, part of the phenol volatilising; by carefully heating it at about 30—35°, the phenol can be almost entirely removed. It melts at 61°. Nitrogen estimations indicate a formula corresponding with 1 mol. urea and 2 of phenol,

$$CO(NH_2)_2,(C_6H_5\cdot OH)_2.$$

J. T.

Condensation of Terephthaldehyde with Hydrocarbons. By H. Oppenheimer (*Ber.*, **19**, 2028—2030).—Griepentroz has lately shown (this vol., p. 887) that although sulphuric acid does not cause the condensation of benzaldehyde with benzene, such a condensation does take place if the mixture of the two substances be heated with zinc chloride. The author finds that if terephthaldehyde is dissolved in strong sulphuric acid, excess of benzene added to the mixture, and the whole heated in closed tubes at 100°, condensation takes place, the compound $CHPh_2\cdot C_6H_4\cdot COH$ being formed. This is a viscous oil which distils with decomposition at 190—195°, solidifies in a freezing mixture, and then melts at − 15°. It forms a crystalline hydrogen sodium sulphite compound, which yields up the aldehyde again when acted on by acids or bases. When treated with silver oxide, the aldehyde is oxidised to *diphenomethylbenzoic acid*, $CHPh_2\cdot C_6H_4\cdot COOH$, a white substance melting above the boiling point of mercury. With stronger oxidising agents (chromic mixture or permanganate), the aldehyde yields *diphenylcarbinolbenzoic acid*, $OH\cdot CPh_2\cdot C_6H_4\cdot COOH$.

L. T. T.

Colouring Properties of Benzidine Azo-dyes. By R. Möhlau (*Ber.*, **19**, 2014—2015).—Bleached cotton-wool is mordanted with benzidine by putting it into a boiling solution of benzidine hydrochloride and continuing the boiling until all the air is expelled. After 24 hours, it is taken out and washed well with boiling and with cold water. When the mordanted cotton-wool is put into a solution of nitrous acid and then into a solution of sodium naphthionate and boiled, Congo-red is formed in the fibre. In a similar manner, chrysamine-yellow is formed when an alkaline solution of salicylic acid is used. The author considers that the importance of so-called benzidine azo-dyes is due to the presence of paradiamidophenyl in the molecule of these substances. N. H. M.

Dinitronaphthylamine. By O. N. Witt (*Ber.*, **19**, 2032—2033).—Referring to Merz and Ris' method for the preparation of orthonitraniline (this vol., p. 872), the author states that he has also found the ammonia method available for preparing dinitronaphthylamine. Dinitronaphthol (prepared by precipitating a boiling aqueous solution of commercial Martius' yellow with hydrochloric acid) is heated with alcoholic ammonia in sealed tubes at 190—200°. The author finds that dinitronaphthylamine melts at 239° (Liebermann and Hammerschlag give 235°). Above 200°, alcohol acts on this compound, yielding a nitramidonaphthol apparently. L. T. T.

Behaviour of β-Dinaphthylamine. By C. Ris (*Ber.*, **19**, 2016—2017).—β-Dinaphthylamine is decomposed by strong hydrochloric acid at 195—205° into β-naphthol and β-naphthylamine.

When β-dinaphthylamine is heated with twice its weight of zinc and ammonium chloride for eight hours at 370° it is converted into β-mononaphthylamine. N. H. M.

α-Naphthyl Phenyl Ketone. By K. Elbs and G. Steinike (*Ber.*, **19**, 1965—1968).—α-Naphthyl phenyl ketone is conveniently prepared by Friedel and Craft's method (compare this vol., p. 461). When heated with sulphuric acid, it is decomposed into benzoic and β-naphthalenesulphonic acids. Bromine in presence of sunlight acts on the ketone with formation of Rospendowsky's monobromide (compare *Compt. rend.*, **102**, 872); it melts at 100·5°.

Dinitromonobromo-α-naphthyl phenyl ketone, $C_{17}H_9OBr(NO_2)_2$, is obtained by dissolving the ketone in fuming nitric acid. It forms small lustrous crystals of a deep yellow colour which decompose at 90° with evolution of gas.

Monobromo-α-naphthyl-phenyl-ketonesulphonic acid is formed when the monobromide is treated with sulphuric acid. It crystallises in lustrous plates melting at 116°.

When the ketone is reduced with zinc and alcoholic solution of hydrogen chloride, the *β-pinacoline*, $CPh(C_{10}H_7)_2{\cdot}COPh$, is obtained. It crystallises from a mixture of alcohol and ether in small, colourless grains melting at 130°. It is decomposed when boiled with alcohol and caustic potash, yielding *dinaphthyl phenyl carbinol*, melting at 160—170°, and benzaldehyde. N. H. M.

Naphthoic Acids. By Å. G. Ekstrand (*Ber.*, **19**, 1982—1989).—When amidonaphthoic acid (m. p. 211—212°; compare Abstr., 1885, 549) is diazotised by adding a solution of potassium nitrite (1 mol.) to a cooled thin paste of the amido-acid (1 mol.) and sulphuric acid (2 mols.), a compound is formed to which the formula $C_{44}H_{29}N_3O_{10}$ is provisionally assigned. It is a brownish-red powder which gives deep red solutions in alkalis; it melts at about 285°. Tin and hydrochloric acid do not seem to act on it.

When nitro-α-naphthoic acid melting at 239° is warmed with fuming nitric acid, dinitronaphthoic acid (m. p. 265°) is formed as chief product together with α-dinitronaphthalene and *dinitro-α-naphthoic acid*, $C_{10}H_5(NO_2)_2{\cdot}COOH$. The latter crystallises in small lustrous needles melting at 215°; it dissolves readily in alcohol and glacial acetic acid, sparingly in benzene and light petroleum. The *ethyl salt* crystallises from alcohol in colourless needles which melt at 137°. *Nitramido-α-naphthoic acid* is obtained by saturating an ammoniacal solution of the dinitro-acid with hydrogen sulphide. It forms yellow microscopic needles.

When dinitro-α-naphthoic acid melting at 265° is reduced in ammoniacal solution with hydrogen sulphide, an intense blue coloration is produced. On adding acetic acid to the solution previously freed from excess of hydrogen sulphide, a deep blue precipitate is formed. This is purified by dissolving it in ammonia and precipitating with acetic acid. The analyses and properties of the compound point to the formula $COOH{\cdot}C_{10}H_5\begin{<}{N \atop |}\!\!>O_2$. It is sparingly soluble in the usual solvents. The salts could not be crystallised.

Trinitro-α-naphthoic acid, $C_{10}H_4(NO_2)_3{\cdot}COOH$, is obtained by warming a solution of the dinitro-compound (m. p. 265°) in a mixture of nitric and sulphuric acids. It crystallises from alcohol, in which it dissolves very readily, in hard needles melting at 236°. The *ethyl salt* crystallises from alcohol in groups of needles; it melts at 191°.

In the preparation of the compound above mentioned, another *trinitro-α-naphthoic acid* is formed. The best yield of this substance is obtained when dinitronaphthoic acid is heated for a long time almost to boiling with a mixture of nitric acid of sp. gr. 1·42 and fuming acid. It crystallises from glacial acetic acid in small hard cubic crystals rather sparingly soluble in alcohol; it melts at 293°. The *ethyl salt* forms needles melting at 150°.

Nitronaphthamide, $NO_2{\cdot}C_{10}H_6{\cdot}CONH_2$, is prepared by heating on a water-bath a solution of α-naphthamide in nitric acid (sp. gr. 1·42) to which some fuming acid has been added. It crystallises from alcohol, in which it is sparingly soluble, in slender needles melting at 280°. When heated with fuming hydrochloric acid at 170°, it is converted into dichloronaphthostyril (compare this vol., p. 715).

N. H. M.

Pyrene. By E. Bamberger and M. Philip (*Ber.*, **19**, 1995—1999; compare this vol., p. 718).—When pyrenic acid (*loc. cit.*) is distilled with lime, *pyrene ketone*, probably of the formula $C_{12}H_8{\cdot}CO$, is obtained; it crystallises from dilute alcohol in lustrous, gold-coloured plates

melting at 141°, and has all the properties of a ketone. The formation of this substance shows that pyrenic acid is a ketonic acid, and that the CO-group cannot have the α-position.

Pyrenic acid is oxidised by dilute potassium permanganate solution with formation of *naphthalenetetracarboxylic acid*, $C_{10}H_4(COOH)_4$; this crystallises in colourless glittering needles; when distilled with lime it yields naphthalene. N. H. M.

Polygonic Acid. By Rademaker (*J. Pharm.* [5], **13**, 140—141).—This acid can be extracted from *Polygonum hydropiper* by treating the plant with water containing a little sodium carbonate; after 24 hours' maceration, basic lead acetate is added to the extractive solution. The lead is precipitated by sulphuric acid, the acid extracted by means of ether, and the ethereal solution evaporated. The residue is then treated with water and the solution filtered, resinous matter remaining on the filter. The filtrate is decolorised by means of animal charcoal, again filtered, and gelatin added to remove tannin, finally the solution is evaporated just to dryness, the residue extracted with ether, and the solution allowed to evaporate slowly. Polygonic acid is obtained in the form of long needle-shaped crystals; its aqueous solution is not precipitated by tannin, nor by a mixture of ferrous and ferric salts, which serve to detect gallic and tannic acids. It is very soluble in water, less soluble in ether, insoluble in light petroleum. It is not decomposed at 100°.

J. T.

Diquinoline-[2′ : 2′] derivatives. By H. Weidel and G. Glaser (*Monatsh. Chem.*, **7**, 308—330).—In a former communication (Abstr., 1882, 70) one of the authors has observed the formation of a disulphonic acid by the action of sulphuric acid and anhydride on the 2′ : 2′ diquinoline; it is here shown that one mono- and two di-sulphonic acids are formed according to the conditions of the reaction. Thus with a mixture of 20 parts acid to one of anhydride, the mono-acid is the principal product, with four parts acid to one of anhydride the α-di-acid, and with a still larger proportion of the anhydride the β-di-acid is formed in the greater quantity.

The *mono-acid*, $C_{18}H_{11}N_2{\cdot}SO_3H$, is a white, crystalline mass consisting of minute needles, characterised by their insolubility in hot water. The *potassium* salt crystallises with 2 mols. H_2O in needles, readily soluble in water; the *copper* salt, with 2 mols. H_2O, is a golden-green insoluble precipitate.

When fused with potash, the potassium salt yields a *hydroxy*-quinoline, which melts at 208° and crystallises in the monoclinic system. It combines both with acids and with bases, and forms double compounds with metallic chlorides. The *potassium* and *lead* salts crystallise in glistening, monoclinic leaflets. The *acetyl*-derivative crystallises in needles melting at 156°, is soluble in water, soluble in alcohol and benzene; it resembles the parent diquinoline in combining with a molecular proportion of methyl iodide. The *α-disulphonic* acid is described in the paper alluded to above; the *potassium* salt crystallises with $5H_2O$ in glistening needles; the *copper* salt with $6H_2O$ is a green crystalline precipitate. The corresponding *dihydroxyquinoline*

forms minute colourless needles, which melt at 239°, and are insoluble in water, alcohol, and benzene, but soluble in xylene. Its compounds with acids and bases are readily decomposed; the *hydrochloride* crystallises in yellow needles, and the *platinochloride* in golden-red leaflets. The *acetyl*-derivative forms glistening rhombohedral crystals, which melt at 169—170°, and are soluble in alcohol, ether, and acetone.

The *β-disulphonic acid* crystallises in minute needles; its *potassium* salt is a crystalline powder, the *copper* salt a blue amorphous precipitate. The corresponding dihydroxydiquinoline is a white crystalline powder, sparingly soluble in most menstrua; it melts above 305°; its *acetyl*-derivative melting at 216° crystallises in the rhombic system. Inasmuch as the *α*-acid when heated with sulphuric acid is converted into the *β*-acid, it would appear that in their formation from diquinoline an intramolecular change occurs, and that the relation between these two acids is similar to that between the *α*- and *β*-sulphocinchonic acids. However, on distillation with zinc-dust both re-form the original diquinoline.

The paper concludes with a description of a practical method for the preparation of diquinoline, and its separation from the simultaneously formed tetrahydrodiquinoline. V. H. V.

Constitution of *α*-Diquinoline. By H. Weidel and H. Strache (*Monatsh. Chem.*, **7**, 280—307).—Hitherto it has not been found possible to determine the constitution of the diquinoline obtained by Weidel (Abstr., 1881) by the action of sodium on quinoline, owing to the difficulty of obtaining well-defined oxidation products. This paper contains a detailed description of the products formed from the diquinoline by oxidation with potassium permanganate; the results obtained show that its constitution is represented by the formula 2′ : 2′. The products formed on oxidation are cyclothraustic, $C_{17}H_{12}N_2O_3$, quinaldinic, $C_{10}H_7NO_2$, hydroxyisocinchomeronic, $C_7H_5NO_5$, and $C_7H_7NO_2$, anthranilic acids. Of these the first, as insoluble, remains attached to the reduced manganese peroxide, and is separated therefrom by passing sulphurous anhydride over the mixture until the peroxide is converted into the sulphate; the product is then exhausted with water. The three remaining acids are separated by their solubility in alcohol and ether.

Cyclothraustic acid,* $C_9NH_6{\cdot}C(OH) : N{\cdot}C_6H_4{\cdot}COOH$, forms aggregates of white woolly needles; it melts at 252°, is sparingly soluble in alcohol, ether, and benzene, soluble in acetic acid. The *calcium*, $(C_{17}H_{11}N_2O_3)Ca$, and *barium* salts are crystalline precipitates. With acetic anhydride, the acid forms a lactonic anhydride, which melts at 196°. On oxidation with potassium permanganate in acid solution, cyclothraustic acid gives the same products as the original diquinoline; but on oxidation in alkaline solution it yields *pyridanthrilic acid*,

$$C_4NH_2(COOH)_2{\cdot}C(OH) : N{\cdot}C_6H_4{\cdot}COOH,$$

derived from cyclothraustic acid by the oxidation of the phenylene residue into the carboxyl groupings. This acid crystallises in mica-

* Cyclothraustic, derived from κύκλος, circle, and θραῦστὸς, broken up.

ceous leaflets which melt at 265—266° with evolution of gas; on further oxidation with alkaline permanganate, it yields isocinchomeronic and anthranilic acids.

α-Hydroxycinchomeronic acid, $C_5NH_2(OH)(COOH)_2$, alluded to above, forms vitreous crystals of the rhombic system, which melt at 287—289° with decomposition; the acid is insoluble in water, alcohol, and ether. It gives no coloration with ferric chloride, and an intense yellow coloration with ferrous sulphate. On this point, as also by the temperature of its decomposition, it is distinguished from its isomerides already known, namely, ammonchelidonic and α-hydroquinolic acids. Its *barium* and *silver* salts crystallise in needles, and are sparingly soluble. When heated at 200° with acetic anhydride, it is decomposed into carbonic anhydride and a hydroxynicotianic acid,

$$OH{\cdot}C_5NH_3{\cdot}COOH\ [OH : COOH = 1 : 2],$$

isomeric with the *hydroxypyridinecarboxylic* acids already known. It crystallises in anhydrous needles, which melt at 256°, and decompose at a higher temperature into carbonic anhydride and hydroxypyridine, $C_5NH_4(OH)$ OH = 1, identical with that obtained by Geigy.

The quinaldinic acid obtained by the oxidation of the diquinoline is identical with that obtained by Skraup from the oxidation of quinaldine, as shown by its physical properties, its water of crystallisation, and crystallographic measurements of its platinochloride. The known constitution of these oxidation products, which are α-substituted derivatives of quinoline and pyridine respectively, show then that the original diquinoline is a 2′ : 2′ compound. V. H. V.

Cocaïne and its Benzoate. By A. Bignon (*J. Pharm.* [5], **13**, 128—129).—The author proposes to employ light petroleum for the extraction of cocaïne. Alcohol and ether are too costly, and have, moreover, the disadvantage of dissolving foreign substances; there is also the risk of decomposing the cocaïne during distillation. The leaves are macerated for 48 hours with sodium carbonate solution, then dried, and treated with light petroleum, which dissolves the cocaïne set free by the alkaline carbonate. After decantation the petroleum is shaken with water containing one-tenth of hydrochloric acid; this takes up the cocaïne, and on allowing it to remain the hydrocarbon separates. The cocaïne salt in this aqueous solution is almost pure, as the hydrocarbon takes up but very little colouring or resinous matters.

To obtain the cocaïne it is only necessary to precipitate by means of sodium carbonate. Cocaïne of good quality should be white, perfectly soluble in alcohol, ether, and hydrocarbons; it should also dissolve in 20 times its weight of water containing one-tenth of hydrochloric acid, and the solution should be transparent. Cocaïne is decomposed on being heated to 100°; it is also decomposed by strong bases, and by moderately concentrated mineral acids.

Cocaïne benzoate, readily obtained by mixing one part of the acid with about three parts of the base, is very soluble: the solution has a strong odour of coca leaves. J. T.

Cholic Acid. By F. Mylius (*Ber.*, **19**, 2000—2009; compare this vol., p. 480).—When a solution of cholic acid in acetic acid is saturated with hydrogen chloride, a *compound*, $C_{24}H_{40}O_5,HCl$, separates in slender needles. It is decomposed by water into its components; and when kept for some hours in contact with the solution from which it is prepared, it gradually dissolves, with formation of *monacetylcholic acid*, $C_{24}H_{39}AcO_5$. When exposed to the air, it deliquesces, and yields a resinous mass. The *diacetyl compound*, $C_{24}H_{38}Ac_2O_5$, is prepared by treating cholic acid with twice its weight of acetic anhydride in the cold. It is a feeble acid, and dissolves very readily in alcohol, ether, and benzene, &c.; it is almost insoluble in water. Its solutions have an intensely bitter taste. The salts are more sparingly soluble than those of cholic acid; the *barium salt* is quite insoluble in water.

Dehydrocholic acid prepared by oxidising cholic acid was found to have the formula $C_{24}H_{34}O_5$, and not $C_{25}H_{36}O_5$ (compare Hammarsten, Abstr., 1881, 625).

The *trialdoxime* of dehydrocholic acid, $C_{24}H_{37}N_3O_5$, is obtained by the action of free hydroxylamine on dehydrocholic acid. It crystallises from alcohol in microscopic plates, which decompose at 270°. It is almost insoluble in water and ether, sparingly soluble in hot alcohol. When warmed with dilute hydrochloric acid, it is decomposed into its constituents.

The results of the experiments described above show that cholic acid contains three alcoholic hydroxyl-groups, of which two are primary alcohol-groups; also that dehydrocholic acid contains three atoms of oxygen, which react with hydroxylamine, of which at least two are aldehydic.

It is probable that bilianic acid, which is formed by further oxidising dehydrocholic acid, has the formula $C_{24}H_{34}O_8$ (compare Latschinoff, this vol., p. 566), and that it is formed by the conversion of two aldehyde-groups of dehydrocholic acid into carboxyl-groups.

N. H. M.

Physiological Chemistry.

Gastric Digestion in the Horse. By H. Goldschmidt (*Zeit. physiol. Chem.*, **10**, 361—390).—After a period of inanition varying from 12 to 36 hours, 18 horses were fed on a diet of known composition (oats, straw, bread, bran); at periods varying from $1\frac{1}{2}$ to $17\frac{1}{2}$ hours afterwards they were killed, and the contents of their stomachs immediately examined. The contents of the portions of the stomach which differ in structure were separately investigated, the points noted being reaction, nature of acid, quantity of acid, of dextrose, and of peptone and dissolved proteïd: artificial digestion experiments were performed on fibrin, white of egg, and starch, with extracts of the mucous membrane of the various parts. The results obtained were as follows:—

1. That the stay of food in the horse's stomach is much longer than has been hitherto supposed. Various experiments are detailed, the object of which was to trace the course the food takes during the peristalsis of the stomach.

2. That the contents of the horse's stomach are relatively very dry; the reason of a few exceptions to this rule is unknown.

3. The course of gastric digestion is divisible into four periods:—(*a*) Amylolysis alone takes place; lactic acid is formed; duration one hour. (*b*) Both amylolysis and proteolysis occur, the latter especially in the region of the fundus, where alone glands which contain oxyntic cells are found; lactic acid and a small amount of hydrochloric acid are present; duration about six hours. (*c*) Stage of local digestion. Amylolytic digestion only occurs in the œsophageal sac, the region of the lesser curvature, and the greater part of the pyloric antrum. This is accompanied by the formation of lactic acid. Proteolytic digestion alone occurs in the region of the fundus, and is accompanied by the formation of hydrochloric acid. This stage lasts as a rule until the next meal; but if this interval is long, a fourth stage (*d*) may occur in which only proteolysis occurs.

W. D. H.

Feeding Cows with "Sections." By Stutzer and Werner (*Bied. Centr.*, 1886, 465—469).—The cows were fed at one time with "sections" (sugar factory waste), at another with mangolds. Full details are given, from which the deductions to be drawn are that the total yield of milk is unaffected by the different foods, but the skim milk produced by sections turned sour sooner than the other, although the butter was better in colour; the "sections" formed a cheaper food than the roots.

E. W. P.

Chemistry of Vegetable Physiology and Agriculture.

Analysis of Bilberries. By B. Borggreve and Homberger (*Bied. Centr.*, 1886, 487—489).

Moisture	9·14 per cent.
Ash	2·48 „
„ sol. in H_2O	1·94 „
Acid (as tartaric)	7·02 „
Extractive	46·10 „
Sugar	20·13 „

Composition of Ash.

K_2O	57·11	Mn_3O_4	2·05
Na_2O	5·16	P_2O_5	17·38
CaO	7·96	SO_3	3·11
MgO	6·11	SiO_2	0·89
Fe_2O_3	1·12		

E. W. P.

Action of Nitre as compared with Ammonium Sulphate. By MÄRCKER (*Bied. Centr.*, 1886, 448—453).—This is a review of some of Lawes and Gilbert's experiments, having for its object the comparative values of these two nitrogenous manures.

The conclusions arrived at are that the supposed prejudicial action of sulphate is not proved, and never occurs under normal conditions of the soil; sulphate is principally adapted for well cultivated lime soils, but it is not so good a manure for roots as for other crops; when equal quantities of nitrogen are employed, then nitre produces a higher yield both of corn and straw with barley and wheat, but the observed difference of yield is not very great (10—15 per cent.). Ammonium sulphate like all other manures is limited in its action by the quantity of the other plant foods in the soil; a relatively larger supply of nitrogen as ammonium sulphate, is necessary to produce a crop of barley, wheat, or potatoes equal to that obtained with a given quantity of nitrogen as nitre: as the nitrogen in the sulphate, by reason of its lesser activity is correspondingly of less value than that in nitre, we may calculate on a good financial result by the use of the cheaper manure, if more of it than of the nitre in proportion is applied: this result will certainly ensue when the ammoniacal nitrogen is one-fourth cheaper than that in the nitre. E. W. P.

Sulphuric Acid as a Manure. By F. FARSKY (*Bied. Centr.*, 1886, 453—455).—Earth was mixed into a compost with various quantities of concentrated and diluted sulphuric acid; this compost was employed as a manure on some of the plots, whilst on others the acid concentrated and diluted was applied direct; the crop was barley, and the highest yield was obtained from the compost plots, but these latter yielded amongst themselves unequal quantities, the heaviest crop being obtained from that compost which had received least acid. As regards those plots to which the acid had been added direct, it was found that the diluted acid was the most satisfactory; but as the acid is costly, no pecuniary advantage accrues from its employment.

E. W. P.

Analytical Chemistry.

Estimation of Cellulose and Wood Gum. By W. HOFFMEISTER (*Landw. Versuchs-Stat.*, **33**, 153—159).—The author has long been engaged in the endeavour to obtain cellulose in a fair state of purity and at the same time economically. His labours being interrupted by illness and other causes, he publishes the present paper to secure priority of discovery.

Schultze's method is not approved, but the following modifications of it are recommended when large quantities of material are operated on. The fat and resins are first removed by any suitable means, the sample is then reduced to the finest possible state of division, a por-

tion treated in a flask with hydrochloric acid of 1·05 sp. gr., and as much potassium chlorate added as is dissolved at 17·5—20°; the flask is then closed and well shaken from time to time. At the end of about 24 hours, the reaction is complete, and the substance has become yellow throughout. It is then diluted with water, and carefully washed on a filter with hot water, again transferred to a flask, digested for one to two hours on a water-bath, again filtered, and washed successively with water, alcohol, and ether. The residue is nearly pure cellulose.

The author agrees with Wieler that the so-called wood gum is only a modification of cellulose. J. F.

Detection of Atropine. By E. Beckmann (*Arch. Pharm.* [3], **24**, 481—484).—Vitali's reaction for atropine depends on its oxidation with concentrated nitric acid and subsequent formation of an intense violet coloration on the addition of alcoholic potash solution, followed by a cherry-red, and final disappearance of the coloration. Veratrine under the same conditions gives similar colour changes. These reactions do not take place with aqueous potash. To distinguish between the two alkaloïds, the following reactions may be employed: —With nitrous acid instead of nitric acid, and an aqueous potash solution instead of an alcoholic solution, atropine gives a reddish-violet coloration, whilst veratrine gives a yellow one. Atropine when boiled for a short time with a mixture of equal volumes of glacial acetic and sulphuric acids gives a brownish-green fluorescent liquid; the solution remains colourless until the brown colour appears. Veratrine gives the same brown-coloured liquid finally, but during the heating passes from colourless through an intense cherry-red colour to the final brown. The fragrant odour produced on heating atropine with sulphuric acid, or with sulphuric acid and potassium dichromate, is not produced by veratrine, but on the addition of the dichromate the latter gives an odour of acid caoutchouc gum. The newer atropine reactions depending on its stronger basic nature as compared with most of the other alkaloïds, do not hold in the case of veratrine. Atropine when heated with hydrochloric acid does not give the red solution yielded by veratrine; and a mixture of atropine and sugar gives yellow and brown, whilst veratrine gives green and blue colours. J. T.

Quantitative Estimation of Nitrogen in Plants. By E. Schulze (*Landw. Versuchs-Stat.*, **33**, 124—145).—The author refers to his previous researches (Abstr., 1881, 312; 1885, 935), the explanations now given are intended to supplement and supply defects in methods formerly described. He enumerates the different nitrogenous substances found in plants in the living cell; besides albumin, nuclein and lecithin are probably present, as also plastin, recently discovered by Reinke and Rodewald; this substance is distinguished from albumin and nuclein by its insolubility in alkalis. Stutzer (Abstr., 1882, 1239; 1885, 827) has placed nuclein in his class of "albuminous matters," a name which he gives to those members of the group soluble in the digestive fluids. Peptones are members of this class, but they exist in plants in such small quantities that they

may be practically disregarded. The percentages of nitrogen contained in the different nitrogenous compounds varies very considerably, averaging in albumin, 15·2—18·7; nuclein, 13—16·4; plastin, 12; lecithin, 1·8; asparagine, 21·21; glutamine, 19·17; hypoxanthine, 41·18 per cent. The number of those substances is large, and when several of them are present it is naturally difficult to assign a regular average percentage or to decide on a common factor. The usual mode of estimating the amount of crude protein in foods, namely, multiplying the nitrogen found by 6·25, assuming thus an average of 16 per cent. of nitrogen in all the substances present, the author believes to be wrong, at all events in many cases; it may not be far from the truth when a certain class of substances are alone present, but it would be much more desirable to be able to estimate the nitrogen in the different groups and adopt a factor for each. The author finds in a process described by Stutzer a mode of obtaining such a result at least approximately: the aqueous extract of the plant is freed from albumin by heating it with a metallic hydroxide, preferably copper hydroxide; xanthine when present is precipitated to a slight extent by this reagent, but the error arising from this must be very small; peptones are also precipitated, but as they occur seldom, and when present are only in small quantity, they may be neglected. The author therefore thinks that for substances of the true protein class the factor 6·25 may be retained. As regards amines and non-protein matters, it is desirable to adopt another factor. Asparagine is the most abundant of this class; it contains 21·21 per cent. of nitrogen, it is sometimes replaced by glutamine with 17·19 per cent., and he recommends 4·71 as the factor which should be adopted for them. At best this is only a careful approximation. Leucine, tyrosine, and other compounds poor in nitrogen may be present in varying proportions. The author recommends Sachsse's method for the estimation of asparagine, but says that when glutamine is also present the two substances cannot be separately estimated. All attempts to obtain exact figures in the nitrogen determinations are rendered difficult by the unstable nature of the combinations and the rapidity with which new compounds are formed, the mere heating of extracts causing decomposition of some of them and the formation of others.

J. F.

Detection of Hæmoglobin in Urine. By C. Rosenthal (*Chem. Centr.*, 1886, 251).—The author has investigated Heller's and Struve's tests for the presence of the blood colouring matter in urine; the former consists in warming with aqueous soda, when the precipitate shows a red coloration. This test gave definite results with a dilution of 1 c.c. blood in 1000 c.c. normal urine; with a dilution twice as great, the test broke down. Struve's test, consisting in the isolation of hæmin from the precipitate occasioned in urine by tannin, is uncertain in its results; the presence of iron, however, in the ash from the ignition of this precipitate, is satisfactory evidence of the presence of hæmoglobin in the urine.

C. F. C.

General and Physical Chemistry.

Velocity of Light in Carbon Bisulphide. By Gouy (*Compt. rend.*, **103**, 244—245).—The author has measured the deviation of red and blue light in passing through carbon bisulphide by means of his method of revolving mirrors (*Compt. rend.*, 1885), special precautions being taken to keep the bisulphide at a constant temperature. The deviation is greatest for the blue rays, the difference being about 5″, which is 0·5 per cent. of the total deviation of the red rays. This result agrees with the author's theory (*loc. cit.*). C. H. B.

Spectrum of Nitrogen at the Negative Pole. By H. Deslandres (*Compt. rend.*, **103**, 375—379).—The author gives drawings of the group of bands in the negative pole spectrum of nitrogen, and of the second group in the positive pole spectrum. The strongest band in the positive pole spectrum, 3372, is equal in intensity to the strongest band in the negative pole spectrum, 3914·6, but at very low pressures the latter band is relatively stronger, and it may therefore be regarded as characteristic of nitrogen at low pressures.

The lines constituting this band are distributed in accordance with the following law:—The intervals from one line to the next, expressed in inverse wave-lengths, are almost in arithmetical progression. This relation was pointed out by Piazzi Smith and Herschel, for 16 lines in the green band in the carbon monoxide spectrum. The author finds that the law holds good in a very large number of cases, but that usually a band consists of several arithmetical series superposed on and interlacing with one another. The number of series is the same for bands of the same origin. The author deduces certain numerical results from this law. C. H. B.

Ultra-violet Spectrum of Cadmium. By L. Bell (*Amer. J. Sci.*, **31**, 426—431).—The ultra-violet spectrum of cadmium having long served as a standard of reference in the measurement of other spectra, an attempt is here made to determine its principal wave-lengths with an accuracy greater than is possible with Cornu's method. The apparatus employed by the author was the great spectrometer in the physical laboratory of the Johns Hopkins University, armed with a grating of 21 feet focal length, and containing in the space of 6 inches nearly 80,000 lines. The great focal length of the grating ensures a perfect focus in photographs over 1 foot in length, and consequently the method of coincidences can be used with great accuracy throughout the ultra-violet. By taking the photographs on Stanley instantaneous dry plates, the author believes that the wave-lengths he determined will be found correct to 1 part in 50,000. The total number of lines accurately determined in the entire spectrum

was 30, the wave-lengths of which are given in a table, with the corresponding values obtained by Hartley and by Cornu.

B. H. B.

Identity of the Reversal Spectrum Zβ with Crookes' Fluorescence Spectrum. By L. de Boisbaudran (*Compt. rend.*, **103**, 113—117).—A mixture of 1 part of terbia with about 13,000 parts of lime shows a brilliant fluorescence in a vacuum with the single green band of the spectrum Zβ, whilst a mixture of 1 part of Marignac's gadolinium with about 11000 parts of lime, gave no fluorescence bands at all. It follows that the fluorescence Zβ obtained in a vacuum in presence of excess of lime is not due, as Crookes supposes, to gadolinium, but must be attributed to the same earth which gives the reversal spectrum Zβ. A mixture of 1 part of terbia with 1145 parts of purified yttria, gave a brilliant fluorescence showing very distinctly the two green bands, with the positions and characters indicated in Crookes' original drawing, whilst a mixture of gadolinia with a somewhat smaller proportion of yttria showed only a trace of the two bands. Other experiments of a similar character led to the same result. The structure and intensity of the green band vary considerably with the nature of the solid substance with which the earth giving the band is mixed.

The band at 6190 in the fluorescence spectrum of yttrium in a vacuum, which Crookes attributes to a new element, seems to be due to the same substance as the red band in the reversal spectrum Zβ. With terbia, which gave brilliantly all the bands in Zβ, the author has measured the position of this band under various conditions, with the following results:—Reversal spectrum in hydrochloric acid solution, 6204; in a vacuum in presence of excess of lime, 6209; in a vacuum in presence of excess of yttria, 6186. Crookes found 6189. The values 6186 and 6189 may be regarded as identical, but they differ markedly from the values 6204 and 6209, although the latter were obtained with the same samples of terbia used in the experiment giving 6186. It is evident that changes in the position and structure of the band are due to changes in the medium in which the substance giving the band is contained. It seems certain that the red band at 6189 in Crookes' original yttria spectrum is due to the earth which gives the red band in the author's reversal spectrum Zβ, and is not characteristic of a new element. C. H. B.

Optical Phenomena of Lead Dithionate. By G. Wyrouboff (*Jahrb. f. Min.*, 1886, ii, Ref., 353).—The author has observed in lead dithionate the optical phenomena described by Klocke (*Jahrb. f. Min.*, 1880, ii, 97). He finds that the planes of the optic axes are not always perpendicular to ∞P, but inclined towards it at a variable angle (30° to 60°). The angle of the optic axes also varies in thin sections of the same plate. Very thin plates, obtained by evaporating a drop of the solution, appear perfectly optically uniaxial. B. H. B.

Connection between Absorption and Photographic Sensitiveness. By J. M. Eder (*Monatsh. Chem.*, **7**, 331—350).—This

paper is a continuation of experiments on the effect of various dyes on the photographic sensitiveness of silver bromide towards the solar spectrum; and on the relation between the maximum decomposition of silver bromide plates, immersed in solutions of these dyes, and the maximum absorption effect of gelatin stained with the same dyes (this vol., p. 405). Among the substances, the effects of which are here examined, are cœrulein, gallein, various reds, furfurins, indulins, and other blues.

It appears from the results that isomeric substances, such as orange R, $SO_3Na{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6(OH)_\alpha$, and acid orange,

$$SO_3Na{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6(OH)_\beta,$$

do not produce the same effect. The former results on the non-coincidence of the maximum decomposition and maximum absorption are also confirmed, the shifting of the former towards the red end corresponding with a difference of wave-length of about 25 millionths of a millimetre.

It is well known that the presence of potassium or other soluble bromide in a silver bromide plate increases the distinctness of the image at the cost of sensitiveness of light; the same effect is also observed with silver bromide plates treated with these dyes.

V. H. V

Effluviography. By D. Tomassi (*Bull. Soc. Chim.*, **45**, 873).—Effluviography is the term applied by the author to the action which the silent discharge has on a sensitised gelatin bromide plate: an image is obtained in complete darkness after an exposure of some minutes' duration, and may be developed in the usual manner; the author considers that this shows that the silent discharge produces the same effects as the ultra-violet rays, and may form a connecting link between the two extremes of the spectrum consisting of what may be called "*electric rays.*" A. P.

Behaviour of Dielectric Liquids under Strong Electric Charges. By G. Quincke (*Ann. Phys. Chem.* [2], **28**, 529—550).—This paper is a continuation of the author's researches on the dielectric constants of liquids (Abstr., 1883, 945). The measurements were made (1) by means of an electric balance, (2) by connecting the charged condensers through a water-column and galvanometer of 20,000 turns. In the first case, $K_p = \frac{G_2}{G_1} \cdot \frac{P_1^2}{P_2^2}$, where G_1, G_2 are the weights in air and the liquid respectively, and P_1, P_2 the corresponding differences of potential. In the second, $K_p = \frac{s_2}{s_1} \cdot \frac{P_1}{P_2}$, where s_1 and s_2 are the deflections of the galvanometer for air and the liquid respectively. In these experiments, high potentials were used. The results show that the dielectric coefficient decreases slightly as the difference of potential increases. The coefficients obtained by the galvanometer method are 10 to 50 per cent. less than those determined by the electric balance, the difference being greater the greater the difference of potential. The author has determined the dielectric

strength of various liquids by causing a spark discharge to pass between curved conductors submerged in the liquids, this being given by the equation $p = \frac{K_p P^2}{8\pi a^2}$, where a equals distance between the conductors. Experiments were also made on the conducting capacity of liquids by connecting one condenser with a Leyden battery at known potential, and the other through a water-column and galvanometer with the earth. The value P/J, where J equals the deflection, was found not to be constant, as in Ohm's law, but decreased as P increased. The value J is subject to variations, probably due to small quantities of dust in the liquids. From curves plotted on results obtained, the author finds the following values for P/a for incipient chemical decomposition.

Oil of turpentine	100	C.G.S.
Naphtha	110	„
Carbon bisulphide	130	„
Ether.....	180	„
Benzene	220	„

H. K. T.

Electrification of Ice by Water Friction. By L. Sohncke (*Ann. Phys. Chem.* [2], **28**, 550—560).—In these experiments, water is driven through a capillary tube formed in ice, platinum electrodes being immersed in the entering and issuing liquid. Whilst water by friction with most solid substances becomes positively electrified, by friction with ice it acquires a negative charge. The deflection of the galvanometer light ray only amounted to from three to six divisions of the scale, whilst a Beetz-Daniell element gave a deflection of 50°.

In a second series of experiments, a jet of water was caused to strike a sheet of ice at an angle. Two electrodes were placed, one where the stream struck the ice, the other farther down in its path. The author considers that these results oppose Edlund's theory (*Ann. Phys. Chem.*, **1**, 161), in which the usual + electrification is due to a straining of the ether caused by the forward motion of the stream of liquid. Tin, steel, and glass, when rubbed against ice produce a + charge in the latter. H. K. T.

Thermoelectric Relations of Electrolytes. By W. Doyle (*Ann. Phys. Chem.* [2], **28**, 574—604).—In these experiments, the liquids whose thermoelectric constants are to be determined are separated from one another by membranes, instead of being in direct contact as in Wild's experiments (*Ann. Phys. Chem.*, **103**, 353), the results so obtained are somewhat higher than those of the latter author. The measurements were made by a Thomson's quadrant galvanometer, a Beetz-Daniell being used for comparison. Readings were taken during rising and falling temperatures.

In the following list, each salt is positive to those to the left of it:—

NH_4Cl, KCl, NaCl, $CaCl_2$, $BaCl_2$, $SiCl_2$, $CuCl_2$, HCl.

The E.M.F.'s are generally higher the greater the difference of temperature. H. K. T.

Relations between Chemistry and Physics. By A. Colson (*Bull. Soc. Chim.*, **46**, 2—6).—The specific heats of isomerides of position—for instance, ortho-, para-, and meta-compounds of the hexacarbon-ring—when multiplied by their specific gravities give constant results.

As these isomeric compounds have the same coefficient of dilatation under constant pressure, the converse of Montier's deduction, that in compounds which have the same coefficient of expansion under constant pressure and volume, the product of the specific heat into the specific gravity is a constant, seems to be true. The author further points out that of two isomerides the denser is formed with the greater development of heat, and will have the lower specific heat. By an application of the above rule, the author shows that metaxylene should be formed more readily than its isomerides, as its specific heat is lower; whilst in the case of the xylene dibromides the para-compound should be most readily formed; theoretical deductions which are borne out by practice. A. P.

Specific Heat of Alloys of Lead and Tin. By W. Spring (*Bull. Soc. Chem.*, **46**, 255—261).—At low temperatures, alloys of lead and tin behave as simple mixtures of their constituents, each element still keeping its specific properties; as the temperature rises, a molecular action takes place, the molecules of each metal being broken down into molecules of simpler construction. This molecular modification increases in rapidity with the rise of temperature, and at a certain point attains its maximum, when the alloy melts, and it is to what the author terms the simplication of the molecules of the metals when heated in intimate contact with one another, that alloys so frequently have a melting point situated below that of either of their component metals. After the alloy is fused, the molecular change becomes less active, and finally, at a certain temperature varying with the composition of the alloy, ceases altogether; the alloy then once more behaves as a mixture of the component metals, each, however, having a more simple molecular structure than that of the separate metals at the same temperature. On cooling a melted alloy, an inverse action takes place. A. P.

Heat of Formation of Hydrogen Selenide. By C. Fabre (*Compt. rend.*, **103**, 131—134).—The heat of formation of hydrogen selenide was determined by measuring the thermal disturbance resulting from the action of the gas or its solution on ferric chloride, hydrogen peroxide, or selenious acid, the values obtained being respectively −18·74, −18·58, and −19·34 cal. From these results, it follows that—

H_2 gas + Se, amorphous = H_2Se gas	develops	− 18·88 cal.
H_2 gas + Se, metallic = H_2Se gas	„	− 13·21 „

C. H. B.

Thermochemistry of Selenides. By C. Fabre (*Compt. rend.*, **103**, 269—270).—*Ammonium Selenide.*—

N_2 gas + $4H_2$ gas + Se metallic = $(NH_4)_2Se$ diss.	develops	+ 44·48 cal.

Ammonium Hydroselenide.—Heat of solution $-9{\cdot}98$ cal.—

N gas + H_5 gas + Se metallic = NH_4HSe solid	develops	+ 28·85 cal.
NH_3 gas + H_2Se gas = NH_4HSe solid	„	+ 29·85 „

Lithium Selenides.—Heat of solution of the anhydrous salt at 20° = + 10·66 cal.—

Li_2 solid + Se metallic = Li_2Se solid	develops	+ 90·6 cal.

The hydrated salt, $Li_2Se,9H_2O$, forms colourless crystals which seem to belong to the rhombic system and alter very rapidly when exposed to air: heat of solution at 17° = − 12·2 cal. C. H. B.

Heats of Formation of Crystallised and Amorphous Selenides. By C. Fabre (*Compt. rend.*, **103**, 345—347).—The author has determined the heats of formation of crystallised selenides produced at high temperatures and of the corresponding selenides obtained by precipitation, by dissolving them in bromine-water and measuring the thermal disturbance. The values given are all referred to metallic selenium and the solid metal:—

		Cal.		Cal.
Ferrous selenide, FeSe,	cryst.	+ 18·44 :	pptd.	+ 15·62
Manganous selenide, MnSe	„	+ 31·14 :	„	+ 27·50
Cobalt selenide, CoSe	„	+ 19·28 :	„	+ 15·20
Nickel selenide, NiSe	„	+ 18·42 :	„	+ 14·8
Zinc selenide, ZnSe	„	+ 40·4 :	pptd. cryst.	+ 34·00
„ „		—	pptd. amorph.	+ 33·6
Cadmium selenide, CdSe	„	+ 26·00 :	pptd.	+ 22·90
Cuprous selenide, Cu_2Se	„	+ 20·84		
Cupric selenide, CuSe	„	—	„	+ 9·70
Thallium selenide, Tl_2Se	„	+ 17·72 :	„	+ 14·72
Lead selenide, PbSe	„	+ 15·76 :	„	+ 12·96
Mercuric selenide, HgSe	„	+ 19·70 :	„	+ 16·00
Silver selenide, Ag_2Se	„	+ 4·72 :	„	+ 2·48

The differences between the heats of formation of the precipitated selenides and those of the corresponding sulphides are less than the differences observed between the heats of formation of the corresponding compounds of the alkaline metals. C. H. B.

Thermochemistry of the Chromates. By P. Sabatier (*Compt. rend.*, **103**, 267—269).—Heat of solution of chromic anhydride at 19° = − 1·9 cal.—

CrO_3 diss. + $\frac{1}{2}K_2O$ diss. = $KHCrO_4$ diss.	develops	+ 13·5 cal.
CrO_3 „ + K_2O „ = K_2CrO_4 „	„	+ 25·4 „

From these results, which differ but slightly from those of Thomsen, it follows that—

$K_2Cr_2O_7$ diss. + K_2O diss. develops + 23·8 cal.

Direct determination gave + 23·0 cal. Berthelot found + 23·2.
Ammonium Chromate.—Heat of solution at 18° − 5·8 cal.—

CrO_3 solid + $2NH_3$ gas + H_2O solid = $(NH_4)_2CrO_4$ solid ..... develops + 46·2 cal.
$(NH_4)_2Cr_2O_7$ solid + $2NH_3$ gas + H_2O solid = $2(NH)_2CrO_4$ solid ..... „ + 35·8 „

Ammonium Potassium Chromate. — Heat of solution at 17° = −10·6 cal.—

$K_2Cr_2O_7$ diss. + $2NH_3$ diss. = $2K(NH_4)CrO_4$ diss. ..... develops + 21·2 cal.
$K_2Cr_2O_7$ solid + $2NH_3$ gas + H_2O solid = $2KNH_4CrO_4$ solid ..... „ + 31·0 „

The direct combination of normal ammonium and potassium chromates in the solid state is accompanied by a very feeble thermal disturbance. C. H. B.

Critical Temperatures and Pressures of some Vapours. By C. Vincent and J. Chappuis (*Compt. rend.*, **103**, 379—381).

	Critical temperature.	B. p.	T − *t*.	Critical pressure.	$\frac{273 + T.}{p}$
Hydrogen chloride.....	51·5°	− 35·0°	86·5	93	3·4
Methyl chloride.....	141·5	− 23·7	165·2	76	5·7
Ethyl chloride	182·5	+ 12·5	170·0	54	8·4
Propyl chloride	221·0	+ 46·5	174·5	49	10·0
Ammonia	131·0	− 38·5	168·5	113	3·6
Methylamine	155·0	− 2·0	157·0	72	5·9
Dimethylamine	163·0	+ 8·0	155·0	56	7·9
Trimethylamine.....	160·5	+ 9·3	151·2	41	10·5
Ethylamine	177·0	+ 18·5	158·2	66	6·8
Diethylamine.....	216·0	+ 57·0	159·0	40	12·2
Triethylamine	259·0	+ 89·0	170·0	30	17·4
Propylamine	218·0	+ 49·0	169·0	50	9·8
Dipropylamine	277·0	+ 97·4	179·6	31	17·7

The difference between the critical temperatures and pressures in a homologous series is not constant but generally increases. Amongst isomeric compounds neither the critical temperature nor the difference between the critical temperature and the boiling point is constant.

The ratio of the absolute critical temperature to the critical pressure increases progressively with the complexity of the molecule in each homologous series, whilst the critical pressure diminishes. The critical pressures of isomerides are not identical, but, like the critical temperatures, increase with the complexity of the substituted molecule. C. H. B.

Vapour-tension of Mercury at ordinary Temperatures. By J. D. Van der Plaats (*Rec. Trav. Chim.*, **5**, 149—183).—The liability

of workmen dealing with mercury to necrosis, and the destruction of plant-life in an atmosphere confined over mercury, offer a sufficiently general indication that at ordinary temperatures the metal is appreciably volatile. On the other hand, the experiments of Faraday seemed to show that below $-7°$ the tension of mercury vapour was inconsiderable, and the experiments of Regnault were apparently confirmatory of this view, until afterwards he proved that daguerreotypes could be developed by mercury vapour below this temperature. Recently Hertz and Hagen have made determinations of the tension of mercury vapour at about 100°, and by means of the mechanical theory of heat deduced expressions for the relation between the temperature and the vapour-tension; at higher temperatures Ramsay and Young have made fresh determinations (Trans., 1886, 37). As interpolation values deduced from the hydrostatic method for low temperatures are unsatisfactory, the author has adopted an absorption method. In principle, the process consists in passing a known volume of purified air saturated with vapour of mercury through absorption tubes filled with finely divided gold. Then from the data of the volume of air, the gain in weight of the absorption tube, and the density of mercury vapour, the tension of the vapour at any particular temperature can be calculated. The sources of error inherent to this method, the possible liability to oxidation of the metal, and the consequent experiments conducted with gases other than air, are discussed in full. As main results the following values were obtained:—

Temperature.	Tension in 0·001 mm.
0°	4·7
10	8·0
20	13·0

These values are not concordant with those recently obtained by Ihmori (this vol., p. 776), in which platinum-black was used, but this substance is not a satisfactory absorbent. V. H. V.

Pressure Curves of Fluids at their Critical Condition. By S. v. Wroblewski (*Monatsh. Chem.*, **7**, 383—405).—Hitherto it has been customary to represent the relation between the volume and pressure of a gas at any given temperatures by curves, known as isothermals. Recently Jamin has proposed to substitute for the volume, its reciprocal the density, which is taken as the ordinate, and the pressure as the abscissa. It is here proposed to trace out by means of curves the relation between the temperature and pressure; an alteration of the former is correlative with an alteration of the latter, if the density remains the same. These lines of equal density are called "isopyknes." It follows that if a system of isopyknes be drawn for an homogeneous isotropic system, the curves in no place cut one another. In this paper, the curves for carbonic anhydride are drawn and described in detail, the constants being taken from the formulæ of Clausius and Sarrau.

Andrews has interpreted the critical temperature as the point above which no liquefaction of the gas is possible, on the ground of the non-formation of a meniscus, and on the course of the isothermal

curve. To the first of these grounds, Jamin has objected in that in the neighbourhood of the critical temperature, owing to the close approximation of the densities of the liquid and gas, the eye is unable to discriminate between the one and the other; and according to the author the course of the isothermal curve proves nothing at all, as the difference between the density of the saturated vapour and that of the liquid condensed becomes infinitesimal. But due consideration has not been paid to the possible latent heat at the critical temperature, and experiments are quoted for the case of nitrogen, in which that liquefied gas passes from the liquid to the gaseous condition without change of pressure; this change of aggregation, however, was not effected without an absorption of heat.

It would appear that the change of a liquid into a saturated vapour at the critical temperature is impossible without a change of pressure or an absorption of heat, however immeasurably small.

If, further, one considers that the molecular forces which condition the state of aggregation of a substance, and which are forces of attraction, are functions of the distance of individual particles, that is, are functions of the density but not of the temperature, there is no reason for the change of aggregation of a substance, so long as its density remains the same. For the several reasons herein discussed, the isopyknal curves are to be preferred to the isothermal.

V. H. V.

The Statical and Dynamical Methods of Estimating Vapour-pressure. By W. Ramsay and S. Young (*Ber.*, **19**, 2107—2114).—Regnault's rule that "with pure substances the curves which show the relation existing between the temperature and pressure of a saturated vapour are identical whether the method employed in obtaining the data used in their projection be the dynamical or the statical," has lately been called in question by Kahlbaum, Schumann, and other chemists. The authors have therefore made a fresh set of careful determinations with pure butyric acid, boiling between 163·55° and 163·8° at 755·6 mm. pressure. The barometer into which the butyric acid was introduced for determining the statical pressure was placed side by side with an exactly similar normal barometer, surrounded by a cylinder of cold water. The experimental barometer was surrounded by a tube connected on the one hand with a boiling vessel containing some of the purified butyric acid, and on the other with a condenser and a mercury manometer to measure the pressure under which the acid was boiling, the temperature being taken by a thermometer hung in the vapour and nearly on a level with the surface of the mercury in the experimental barometer. The barometers and the manometer could be read to 0·1 mm. by means of mirror scales.

The following results were obtained:—

Temperature.	Pressure in barometer tube.	Pressure on boiling liquid as shown by manometer.	Temperature.	Pressure in barometer tube.	Pressure on boiling liquid as shown by manometer.
	mm.	mm.		mm.	mm.
66·5°	12·75	12·85	111·5°	119·55	118·3
76·15	21·9	22·75	117·8	152·75	151·55
85·85	36·85	36·9	123·1	187·7	186·5
93·0	51·9	51·95	127·4	222·9	221·9
99·3	70·25	69·8	133·7	281·1	281·45
105·1	90·65	90·0	—	—	—

It will be seen that the numbers obtained by the two methods were practically identical, the slight discrepancies observed being due to the fact that the butyric acid employed was not of absolutely constant boiling point, a condition which militates strongly against the accuracy of the statical method. It is thus clear that Regnault's rule is correct.

The authors ascribe the different results obtained by Kahlbaum to the following causes:—(i) His use of impure substances. (ii) His having taken as correct the temperatures shown by the thermometer in the vapour when the temperature of the surrounding air was higher than that of the vapour; for instance, with alcohol, benzene, &c., at low pressures. Under these conditions, as Regnault showed, the thermometer is heated by radiation from the air, and must be dipped into the boiling liquid to obtain the correct temperature. (iii) Because, as Kahlbaum himself states, no special care was taken in carrying out the experiments, barometer and thermometer readings, &c., being uncorrected. L. T. T.

Boiling Points and Specific Volumes of the Ethereal Salts of the Normal Fatty Acids. By R. Gartenmeister (*Annalen*, **233**, 249—315). — The following are the results of the author's determinations of the boiling points, specific gravity, and specific volume of a number of ethereal salts:—

	B. p. at 760 mm. (corr.).	Sp. gr. at 0°.	Sp. gr. at b. p.	Volume at b. p.	Sp. vol.
Methyl formate.....	32·5°	1·0009	0·9554	1·0488	62·7
Ethyl „	55·0	0·9445	0·8725	1·0825	84·6
Propyl „	81·0	0·925	0·827	1·118	106·2
Butyl „	106·9	0·9108	0·7972	1·1425	127·6
Amyl „	130·4	0·9018	0·7692	1·1723	150·5
Hexyl „	153·6	0·8977	0·7484	1·1995	173·3
Heptyl „	176·7	0·8937	0·7308	1·2229	196·7
Octyl „	198·1	0·8929	0·7156	1·2477	220·3
Methyl acetate	57·3	0·9643	0·8873	1·0868	83·2
Ethyl „	77·5	0·9253	0·8272	1·1182	106·1
Propyl „	101·8	0·9093	0·7934	1·1463	128·4

	B. p. at 760 mm. (corr.).	Sp. gr. at 0°.	Sp. gr. at b. p.	Volume at b. p.	Sp. vol.
Butyl acetate.....	124·5°	0·9016	0·7683	1·1734	150·6
Amyl „	147·6	0·8948	0·7461	1·1992	173·8
Hexyl „	169·2	0·8902	0·7267	1·225	197·7
Heptyl „	191·3	0·8891	0·7134	1·2462	221·0
Octyl „	210·0	0·8847	0·6981	1·2672	245·8
Methyl propionate....	79·5	0·9403	0·8393	1·1203	104·6
Ethyl „	98·8	0·9114	0·797	1·1434	127·7
Propyl „	122·6	0·9023	0·7719	1·169	149·9
Butyl „	145·4	0·8953	0·7489	1·1955	173·2
Heptyl „	208·0	0·8846	0·6946	1·2736	247·1
Octyl „	226·4	0·8833	0·686	1·2876	270·5
Methyl butyrate	102·3	0·9194	0·8026	1·1455	126·7
Ethyl „	120·9	0·9004	0·7689	1·171	150·5
Propyl „	143·2	0·8929	0·7455	1·1981	174·0
Butyl „	165·7	0·8878	0·7264	1·2222	197·8
Amyl „	184·8	0·8832	0·7092	1·2454	222·3
Hexyl „	205·1	0·8825	0·6963	1·2674	246·4
Heptyl „	225·2	0·8827	0·6869	1·285	270·2
Octyl „	242·2	0·8794	0·6751	1·3028	295·6
Methyl valerate.....	127·3	0·9097	0·7767	1·1713	149·1
Ethyl „	144·7	0·8939	0·7443	1·2010	174·3
Propyl „	167·5	0·8888	0·7264	1·2236	197·8
Butyl „	185·8	0·8847	0·7095	1·2465	222·1
Amyl „	203·7	0·8812	0·6982	1·2621	245·8
Hexyl „	223·8	0·8797	0·6823	1·2893	272·0
Heptyl „	243·6	0·8786	0·6708	1·3097	297·4
Octyl „	260·2	0·8784	0·6618	1·3272	322·6
Methyl caproate	149·6	0·9039	0·7536	1·1994	172·2
Ethyl „	166·6	0·8888	0·7269	1·2227	197·7
Propyl „	185·5	0·8844	0·7097	1·2462	222·2
Butyl „	204·3	0·8824	0·6978	1·2646	246·0
Heptyl „	259·4	0·8769	0·6594	1·3298	323·9
Octyl „	275·2	0·8748	0·6509	1·3440	349·6
Methyl heptylate	172·1	0·8981	0·7325	1·2261	196·2
Ethyl „	187·1	0·8861	0·7105	1·2471	221·9
Propyl „	206·4	0·8824	0·6965	1·2670	246·5
Butyl „	225·1	0·8807	0·6839	1·2878	271·3
Heptyl „	274·6	0·8761	0·6496	1·3488	350·2
Octyl „	290·4	0·8757	0·6419	1·3651	376·2
Methyl octylate.....	192·9	0·8942	0·7163	1·2483	220·1
Ethyl „	205·8	0·8842	0·6980	1·2668	245·9
Propyl „	224·7	0·8805	0·6867	1·2823	270·3
Butyl „	240·5	0·8797	0·6745	1·3042	295·9
Heptyl „	289·8	0·8754	0·6405	1·3668	377·0
Octyl „	305·9	0·8755	0·6318	1·3858	404·3
Methyl nonylate	213·5	0·8918	0·7024	1·2696	245·7

The following conclusions are deduced from these results :—

1. The difference between the boiling points of the methyl and octyl salts of the same acid diminishes as the acid grows richer in carbon, and the difference between the boiling points of a formate and octylate of the same alcoholic radicle decreases with an increase of carbon in the alcohols.

As a rule, formates have a higher boiling point than the metameric methyl salts. The acetates boil at a higher temperature than the metameric ethyl salts. The difference between the boiling point of an acetate and a formate is greater than that between the methylic and ethylic salt.

Represent the boiling points of the metameric ethers as co-ordinates, and let their abscissæ indicate the number of carbon-atoms in the alcoholic radicles, then the boiling points form first a descending and afterwards an ascending curve. The starting point lies lower than the final point. As a general rule, with few exceptions, those salts which contain the same number of carbon-atoms in the alcohol and in the acid radicle occur at the bottom of the curves. As a general rule, the specific gravities of the ethereal salts at 0° exhibit a similar periodicity. Generally in the case of metameric ethers, the highest boiling point corresponds with the greatest density, and a large difference between the boiling points of two salts is accompanied by a large difference between their densities. The formates are an exception to this rule, for although their boiling points are higher than those of the metameric methyl salts, their densities are always lower. The specific gravities at the boiling point obey the same laws as the densities at 0°. The difference between the specific volume of the methyl and octyl salt of the same acid and the difference between the formate and octylate of the same alcohol increase with the number of carbon-atoms.

The specific volumes of metameric ethereal salts seldom exhibit a greater difference than 1·5. Methyl salts have a smaller sp. vol. than the metameric formates. Propyl acetate and butyl acetate exhibit larger sp. vols. than ethyl and propyl propionates.

The author's results are directly opposed to Schiff's conclusion (Abstr., 1883, 1044), namely, that in groups of isomeric ethers of analogous constitution, the molecular volumes increase and the boiling points rise as the number of carbon-atoms increase in the acid radicles, and diminish in the alcoholic radicles. Städel's statement (*ibid.*, 302) that in a group of isomerides the substance with the lowest boiling point will have the greatest sp. vol., is confirmed by the author, except in the case of the formates.

With regard to the expansion of metameric ethereal salts, the author finds that the formates exhibit the least expansion; they are followed by the methyl salts. The metameric ethers occupying an intermediate position between these two classes have almost all the same rate of expansion, except the acetates, which always expand a little less than the ethyl salts.

As a general rule, those ethereal salts which exhibit the highest boiling points possess the lowest rates of expansion. W. C. W.

Transition Temperature in Chemical Decomposition. By J. H. VAN'T HOFF and C. M. VAN DEVENTER (*Ber.*, **19**, 2142—2153).—From theoretical grounds (see Van't Hoff's "*Études de dynamique chimique*," 139—148), it was probable that, beyond the phenomena of chemical equilibrium already studied, there is another class of somewhat similar phenomena dependent on temperature, corresponding in

some measure with physical melting and solidification. This was rendered still more probable, firstly, by the well-known fact that where a substance crystallises in two distinct forms, one of these forms is incapable of existing above a certain definite temperature; secondly, by the fact of Glauber's salt ($Na_2SO_4,10H_2O$) melting at 33°, but at the same time depositing the less hydrated salt, Na_2SO_4,H_2O, and by many other phenomena. As these phenomena, however, might be considered as physical, the authors have sought for examples of the same character which should be unmistakably of a chemical nature.

When a solution of sodium and magnesium sulphates in molecular proportions is allowed to crystallise (care being taken to prevent supersaturation), a mixture of the two sulphates crystallises out if the temperature is below 21·5°, but if above that temperature the double salt astrachanite ($Na_2MgS_2O_8,4H_2O$) separates. If astrachanite is finely powdered and mixed with water in the proportion $Na_2MgS_2O_8,4H_2O : 13OH_2$, this thin magma remains liquid above 21·5°, but below that temperature rapidly solidifies to a solid mass, composed of a mixture of the two salts, $Na_2SO_4,10H_2O$ and $MgSO_4,7H_2O$. If, on the other hand, molecular proportions of finely powdered Glauber's and Epsom salts are mixed and allowed to stand at a temperature below 21·5°, no formation of astrachanite will take place, even if a few crystals of that substance have been added. But if the temperature is allowed to rise above 21·5° a gradual formation of astrachanite takes place, water is liberated, and the mass becomes moist. From the specific gravities of the respective substances (astrachanite 2·25, Epsom salts 1·69, Glauber's salt 1·48, water 1), it is clear that the formation of astrachanite must be accompanied by increase in volume. This gave a good means of observing the transition temperature. The finely powdered mixture of the two salts was introduced into the bulb of a dilatometer, the latter being then exhausted and filled with oil. When the bulb was now slowly heated, the oil level rose gradually, but regularly, as the oil expanded, until the temperature reached 21·5°, when a much greater rise took place. Of course the formation of the astrachanite is slow, and therefore to get good results the temperature of the bath should be raised a degree or two and then be kept constant until the oil level has ceased to rise. When the level has ceased rising at 21·5° or 22° (this requires several hours) a further rise in temperature only causes the slow rise of the oil level due to the expansion of the oil. When the temperature is allowed to fall, the level descends slowly and regularly till a temperature of about 21·5° is reached, when there is a great fall (due to the breaking up of the astrachanite and reformation of Glauber's and Epsom salts), and then a still further reduction of temperature is only followed by the normal fall of level. A similar proof of this transition temperature is given by the ratio of solubility, and also by the varying vapour-tensions, at varying pressures.

Similar phenomena are observed with sodium ammonium racemate. Recent researches have shown that when a solution of this substance is allowed to crystallise below 28° no racemate is formed, but only a

mixture of sodium ammonium dextro- and lævo-tartrates; if, however, crystallisation takes place above 28°, sodium ammonium racemate alone is formed. The authors have in this case obtained results similar to those found with astrachanite. Powdered sodium ammonium racemate mixed with water in the proportion $Na_2(NH_4)_2C_8H_8O_{12},2H_2O : 6H_2O$ remains liquid above 28°, but solidifies below that temperature to a mixture of the lævo- and dextro-tartrates, $Na(NH_4)C_4H_4O_6,4H_2O$. On the other hand, a dry mixture of the tartrates remains unchanged below 28°, but above that temperature gradually changes to the racemate, becoming at the same time moist from the water liberated. Dilatometer experiments showed the same transition temperature very plainly. Similar results were obtained with calcium copper acetate, $CaCu(C_2H_3O_2)_4,8H_2O$. This compound exists as a blue salt at ordinary temperatures, but at 70° is resolved into its constituents, $Ca(C_2H_3C_2)_3,H_2O$; $Cu(C_2H_3O_2)_2,H_2O$, and $6H_2O$. The dilatometer gave similar but not very marked results.

Finally, the authors find that by taking a mixture of magnesium sulphate and sodium chloride, in the proportions required for the equation $2MgSO_4,7H_2O + 2NaCl = Na_2Mg(SO_4)_2,4H_2O + MgCl_2,6H_2O + 4H_2O$, the state represented by the left-hand side of the equation is only permanent at temperatures below 31°, the state shown by the right hand only at temperatures above 31°. This is again clearly shown by the dilatometer. This last instance is clearly a chemical intramolecular change, even if the others be only regarded as molecular. L. T. T.

Determination of Molecular Weights of Organic Substances by the Lowering of Freezing Point of their Solutions. By E. Paternò and R. Nasini (*Gazzetta*, **16**, 262—275).—The recent researches of Raoult (Abstr., 1884, 952, and 1885, 858, &c.) have established the law that the molecular weight of a carbon compound is equal to the quotient of a constant by the coefficient of reduction of the freezing point. The constant value of the quotient varies with the nature of the compounds, which are divisible into two principal classes, namely, those which contain the hydroxyl-group and those which do not; for the former it is about double as great as for the latter. If this law were general, it might be applied to determine the molecular weight of substances which are decomposed when converted into vapour, and would be especially advantageous in those cases in which a polymeric modification is thus reduced to a simpler molecule. In this paper the particular cases of aldehyde and paraldehyde, of acetonitrile and cyanomethine, and of cyanamide and dicyandiamide are studied: some of the results are given below:—

Substance.	Molecular reduction.	Substance.	Molecular reduction.
Aldehyde, C_2H_4O	19·22	Acetonitrile, $CH_3{\cdot}CN$ ..	18·61
Paraldehyde, $(C_2H_4O)_3$..	19·24	Cyanomethine, $(CH_3{\cdot}CN)_3$	9·67
Cyanamide, CN_2H_2	16·28	Do., concentrated solution	5·67
Dicyandiamide, $(CN_2H_2)_2$	15·54		

The values obtained for the substances in the first column are in

accordance with the law, but those for cyanomethine vary irregularly with the concentration of the solution.

Determinations are also given of some complex carbon compounds, the results of which are adduced:—

Substance.	Molecular reduction.
Lapachic acid, $C_{15}H_{14}O_3$	46·27
Lapacone, $C_{15}H_{14}O_3$.....	43·10
Picrotoxin, $C_{30}H_{34}O_{13}$ }	109·14 }
or $C_{12}H_{14}O_5$ }	43·15 }
Picrotoxin hydrate, $C_{15}H_{18}O_7$	44·98
Santonide, $C_{15}H_{18}O_3$	47·36

The results obtained for picrotoxin agree more nearly with the formula $C_{12}H_{14}O_5$, proposed by Barth and Kretschy (Abstr., 1882, 412), than with $C_{30}H_{34}O_{13}$, that proposed by Paternò and Oglialoro (Abstr., 1881, 440). It would seem that lapacone is not a polymeric modification of lapachic acid (Abstr., 1883, 213), inasmuch as their molecular reductions of the freezing points are nearly equal.

V. H. V.

Cohesion and Cohesion Figures. By W. Ackroyd (*Chem. News*, **54**, 58).—The author suggests the probability that the solubility of allied groups of compounds in regard to any given solvent, under constant conditions of temperature, conform to laws similar to the periodic law of Newlands and Mendeléeff, and arguments are given in support of the suggestion. When a liquid of high sp. gr. falls into a liquid of lower sp. gr., as is well known, submergence cohesion figures (or vortex rings) are formed; now when molten sulphur heated beyond the viscous state is allowed to fall into water, the drops endeavour to take this form of vortex rings, and in this way therefore solidified vortex rings of plastic sulphur are obtained. The author explains his reasons for regarding these as vortex rings by comparing the conditions of formation with the conditions of formation of aërial vortex rings, and showing their resemblance.

D. A. L.

Fluidity of Absolute and Diluted Acetic Acid. By K. Noack (*Ann. Phys. Chem.* [2], **28**, 666—684).—For these experiments pure aqueous acetic acid was taken, its percentage composition determined from its freezing point, and the necessary quantities of water then added. The author uses the formula $F = F' + \frac{F'^2 vs}{2^{10/3}\pi lz}$ for the flow of liquids through capillary tubes where F equals the corrected, F' the uncorrected fluidity, v the volume of liquid passed, s its specific gravity, l the length of the capillary, and z the time of flow. For distilled water he finds $F' = 55{\cdot}218 + 2{\cdot}0484t + 0{\cdot}007847t^2$, $F = 55{\cdot}557 + 2{\cdot}0615t + 0{\cdot}008306t^2$; for acid of 98·52 per cent. $F = 42{\cdot}371 + 1{\cdot}3498t$.

Curves are also constructed for varying strengths of acid, and also

for the same acid strength with varying temperatures. The influence of temperature is greatest with water, and decreases on addition of acid. A minimum of fluidity is found with 77 per cent. acid represented by $C_2H_4O_2 + H_2O$. H. K. T.

Variations in the Solubility of Chlorides in Presence of Hydrochloric Acid. By G. Jeannel (*Compt. rend.*, **103**, 381—384).—The solubility of potassium chloride in presence of hydrochloric acid does not obey Engel's law (this vol., p. 503). It varies continuously, and diminishes as the proportion of hydrochloric acid increases, but the sum of the equivalents of potassium chloride and hydrogen chloride does not remain constant. If, however, the water is also taken into account, it is found that the sum of the equivalents of the three substances remains constant, and is equal to about 1043.

If similar calculations are made with Engel's numbers for other chlorides it is found that the following law holds good in all cases: the solubility of chlorides in water in presence of hydrochloric acid varies in such a manner that the sum of the equivalents of salt, acid, and water in the solution remains practically constant at the same temperature whatever the nature of the chloride. This law is not absolutely true, but the divergences are only small. Usually the sum of the equivalents slightly increases as the proportion of acid increases, attains a maximum, and then very slowly diminishes.

C. H. B.

Water of Crystallisation. By W. W. J. Nicol (*Chem. News*, **54**, 53).—Looked at from a thermochemical point of view, the results of Thomsen, Meyer, and Ostwald prove that water of crystallisation cannot be attached to the salt in solution, or if it is, no heat is evolved on union more than with solvent water. For example, the heat of neutralisation of the solution of the alkaline and alkaline earthy bases in hydrochloric or nitric acids, has a mean value of 27,640 cal. within very narrow limits, irrespective of the condition of the salts in the solid state, some of which are anhydrous, and some contain water of crystallisation. D. A. L.

Crystals containing Mixtures. By F. Herrmann (*Ber.*, **19**, 2235—2239).—When equal weights of ethyl quinonedihydroparadicarboxylate (c), which crystallises in well-formed rhombic crystals, and ethyl succinosuccinate (s), which forms triclinic crystals, are dissolved in ether, the solution yields a mixture of triclinic and rhombic crystals in the proportion of about 3 : 7. Both crystals consist of a mixture of the two ethyl salts. When the proportion of the amount of the ingredients is within the limit $s > (s : c) > \frac{1}{2}$, crystals of both forms are obtained; the triclinic crystals have the composition $8s + 1c$, and melt at 124·5°; the rhombic crystals have the composition $1s + 2c$, and melt at 127°. The mixtures in which $(s : c) > 8$ give only triclinic crystals, and mixtures in which $(s : c) < \frac{1}{2}$ yield only rhombic crystals. N. H. M.

Atomic Volumes and Specific Volumes. By W. Lossen (*Annalen*, **233**, 316—326).—The author points out that Kopp's law

of atomic volumes is no longer tenable. The specific volume of a compound depends not only on its empirical composition but also on its rational constitution. The atomic volume of an element is different in different compounds. Kopp's statement that the volume of CH_2 is 22 is inexact. In an homologous series, a difference of CH_2 in the formula corresponds with a regularly increasing difference of volume. Kopp's assumption that 1 atom of C can replace 2 atoms of H without alteration of volume is only true in certain cases.

W. C. W.

Division of a Base between Two Acids. By P. Sabatier (*Compt. rend.*, **103**, 138—141).—According to thermochemical data, chromic acid behaves towards alkalis as a bibasic acid with two unequal functions. The energy of the first function, which corresponds with the formation of dichromates, is surpassed only by that of sulphuric acid, approximates closely to that of hydrochloric acid, and is distinctly superior to that of carbonic, acetic, and even phosphoric acids. The second function, or the acid function of the dichromates, is inferior to that of hydrochloric acid, hydrogen potassium sulphate, acetic acid, and the first function of carbonic and phosphoric acids, but is superior to the acid function of potassium hydrogen carbonate and the third function of phosphoric acid.

The author has investigated the action of various acids on solutions of normal potassium chromate by comparing the colour of the liquid with the colours of a series of previously prepared mixtures of the dichromate and normal chromate. With hydrochloric acid, both functions of sulphuric acid, and the first functions of phosphoric and trichloracetic acids displacement is practically complete. With acetic acid and the three equal functions of citric acid, the action does not proceed quite so far. It is still less with the first function of carbonic acid and the second function of phosphoric acid, whilst the second function of carbonic acid, boric acid, and the third function of phosphoric acid have very little action at all. If the normal chromate is treated with an excess of solid boric acid, there is considerable formation of dichromate, owing to the production of an insoluble acid borate, the precipitation of which tends to make the action complete.

Whenever the function of the reacting acid, as measured by thermochemical data referred to the solid state, is superior to that of the dichromate, this superiority is shown by the total action exerted on the neutral chromate by a small quantity of the acid, secondary reactions being practically without influence. This is seen in the graphic representation of the reaction, all the curves at their origin being tangent to the right line of total decomposition. It shows at once the number of functions of each acid which are superior to the acid function of the dichromate. Oxalic acid has two, citric acid three, phosphoric acid two, carbonic acid one, boric acid none.

These results afford further proof of the value of thermochemical data referred to the solid state, and they also show that Thomsen's theory of a modulus for each acid, independent of thermochemical data, cannot be sustained. C. H. B.

Chemical Fractionation. By W. Crookes (*Chem. News*, **54**, 131—133).—Fractionation is resorted to for the separation of substances which are almost identical in chemical properties. Broadly speaking, the operation consists in utilising a reaction in which there is most likelihood of a difference in the behaviour of the elements under treatment; the reaction is performed in an incomplete manner, so that only a certain fraction of all the bases present is precipitated. Then the portions separated in this manner are re-treated, and by working systematically in this way the minute chemical difference is made to accumulate until it becomes perceptible by a chemical or physical test.

Chemical processes are used for fractionation, and they have to be varied according to the substance under examination. When a certain process ceases to act in the manner required, another process must be resorted to. It is shown that for the separation of several substances a number of processes must be used, in fact n bodies require at least $n - 1$ processes. For the separation of earths, fractional precipitation by ammonia is generally adopted; there are three methods of procedure. A series of bottles is used in all. In one method $\frac{1}{3}$ of the equivalent quantity of ammonia is added to the contents of a bottle, the precipitate allowed to settle, and is filtered off, the solution is treated in a similar manner with another $\frac{1}{3}$ of ammonia, and then all the bases still in solution are precipitated, each precipitate is put into its proper bottle, and subsequently goes through a similar series of operations. In another method $\frac{2}{3}$ of the bases present in a bottle are precipitated, the filtrate moving two places to the right, the precipitate going one place to the left, and so on. In a third method, the one adopted and introduced by the author, half the equivalent of precipitant is added at once. When a great number of earths are to be separated the following plan is sometimes adopted: ammonia sufficient to precipitate $\frac{9}{10}$ of the earths is added, then acid to dissolve $\frac{8}{10}$, then ammonia to precipitate $\frac{7}{10}$, and so on until the required proportion of precipitate is obtained. Nitric acid is the best acid to use, and from time to time (in order to avoid the interference of accumulation of ammonium nitrate), the bases are precipitated, ignited and redissolved. The amount of earths present is determined by titration before each addition of a precipitant. Separation by fractionation of distinct substances such as the earths in gadolinite or samarskite is not difficult, as separate chemical processes are available, but to separate the constituents of yttrium, simple straightforward fractionation continued steadily even for years is the only plan. To hasten operations, when a particular constituent has concentrated in certain bottles, these may be removed from the main series and subjected to fractionation by themselves. Working with samarskite earths, fractional precipitation with oxalic acid separates first erbia, holmia, and thulia, then terbia, and finally yttria; in fact it is the only method capable of separating small quantities of terbia from yttria. Fusing the nitrates separates ytterbia, erbia, holmia, and thulia from yttria, but does not work so well in presence of terbia; it is the only method known for separating ytterbia from yttria. The relative merits of the various methods of separation noted above are fully criticised.

D. A. L.

Decomposition of Chlorides in Dilute Solutions. By G. Foussereau (*Compt. rend.*, **103**, 248—250).—The author has investigated the decomposition of several chlorides in aqueous solution by means of the method already applied to solutions of ferric chloride (this vol., p. 844).

Aluminium chloride is decidedly more stable in presence of water than ferric chloride. With a dilution of $\frac{1}{1333}$, the resistance does not vary between 0° and 80°, but at 100° it reaches a limit equal to 0·93 of its original value. If the solution is allowed to cool and is left at the ordinary temperature, the resistance re-attains its original value in about 15 days. With a dilution of $\frac{1}{2780}$, the resistance alters distinctly at the ordinary temperature, and at 100° a limit equivalent to 0·47 of the original resistance is attained in less than 10 minutes. The action of hydrochloric acid is the same as in the case of ferric chloride.

Magnesium chloride is much more stable than aluminium chloride, but seems to be slightly dissociated in very dilute solutions.

Rhodium sodium chloride is distinctly altered with a dilution of $\frac{1}{100}$, but the change takes place very slowly at the ordinary temperature. With a dilution of $\frac{1}{1077}$, the resistance diminishes from 45·8 to 34·7 after standing for three months at the ordinary temperature, and if the solution is heated to 100° the resistance diminishes to 20·7—21·7.

A solution of platinic chloride, unlike the preceding solutions, is affected by light, which although it does not alter the final result accelerates the rate at which the change takes place. With a dilution of $\frac{1}{1593}$, the resistance diminished from 26·3 to 19·6 in about seven days in the dark, whilst in daylight the change was complete in five and a half hours, and in less than an hour in direct sunlight. At 100°, the influence of light is still more marked.

Solutions of auric chloride are also affected by light, and alter very rapidly. In daylight, the limit is reached in a few minutes, whilst in the dark the change requires one to two days according to the concentration of the solution. At 100°, as in previous cases, the alteration of resistance is still more marked. The reverse reaction which takes place on cooling is likewise accelerated by the action of light.

C. H. B.

Etherification by Double Decomposition. By G. Bertoni (*Gazzetta*, **16**, 175—182).—In this paper some general remarks are introduced on the phenomenon of etherification, and on the views expressed by Berthelot and others that the analogy between the ethereal and metallic salts is only superficial, as the former are only produced under special conditions such as increase of temperature and pressure, whilst the latter are formed instantaneously. It is here shown that the preparation of ethereal salts of nitrous acid can be performed as a lecture experiment, namely, by the decomposition of glyceryl trinitrite with alcohols, thus: $C_3H_5(ONO)_3 + 3ROH = 3RONO + C_3H_7(OH)_3$, a subject already investigated by the author (this vol., p. 217). The alcohol is added gradually to the glyceryl trinitrite contained in a test-tube kept cool by ice; then the contents are agitated whereby an emulsion is formed, but this separates finally

into two layers, the upper of which, of a yellow colour, is the ethereal salt of nitrous acid; this is washed with water and finally digested over anhydrous calcium nitrate. In such cases as that of ethylene glycol, the ethereal salt of which is soluble in the aqueous glycerol, its formation is not so easily shown, but the ethereal salt can be readily extracted from the product by means of ether. V. H. V.

Lecture Experiments. By F. C. G. Müller (*Ber.*, **19**, 2175—2179).—A thermometer containing sulphuric acid blackened with sugar is recommended, as it is readily seen; sulphuric acid expands regularly, and has a coefficient of expansion $3\frac{1}{2}$ times greater than that of mercury. A lecture galvanometer and method for demonstrating the principle of the constant galvanic chain are described with sketches. N. H. M.

Inorganic Chemistry.

Electrolysis of Hydrogen Fluoride. By H. Moissan (*Compt. rend.*, **103**, 202—205, and 256—258; see this vol., p. 849).—The apparatus consisted of a platinum **U**-tube with fluorspar stoppers and platinum delivery tubes, the positive electrode consisting of an alloy of platinum with 10 per cent. of iridium. Potassium hydrogen fluoride, prepared by Fremy's method, was dried at 100°, and then over sulphuric acid and potash in a vacuum. The salt thus prepared is much less deliquescent than the normal fluoride. The dried salt was heated in a platinum retort, and the hydrogen fluoride condensed in a receiver cooled with ice and salt. The liquid was then introduced into the **U**-tube, cooled with methyl chloride boiling at − 23°, and subjected to the action of a current from 20 large Bunsen's elements coupled in series. Any small quantity of water present is soon decomposed with liberation of ozone at the positive pole, but as the water disappears the resistance of the liquid rapidly increases, until, when the hydrogen fluoride is perfectly pure a current of even 25 ampères no longer passes. In order to obtain the necessary conductivity, a small quantity of perfectly dry potassium hydrogen fluoride is dissolved in the liquid. Under these conditions hydrogen is given off at the negative pole, whilst at the positive pole a colourless gas is evolved in which crystallised silicon, adamantine boron, arsenic, antimony, sulphur, and iodine take fire spontaneously and immediately. This gas decomposes water with formation of ozone and hydrogen fluoride, but attacks metals much less readily, probably owing to the fact that a superficial layer of fluoride is first formed, and this protects the metal from further action. Powdered iron and manganese when gently heated burn in the gas with production of a shower of sparks. Organic compounds are violently attacked, alcohol, ether, benzene, terebenthene, and petroleum taking fire spontaneously when brought in contact with the gas. When the gas is mixed with hydrogen, even in

the dark, combination takes place with a violent detonation, and hydrogen fluoride is formed.

A mixture of hydrogen fluoride with ozone produces none of these reactions. In order to ascertain if the gas were fluorine or hydrogen perfluoride, the electrolysis apparatus was connected with a platinum tube containing potassium fluoride to remove traces of hydrofluoric acid, and this was connected with another platinum tube which contained a weighed quantity of iron wire, and terminated in an apparatus for collecting any gas which might issue from the end of the tube. Arrangements were also made for collecting the hydrogen evolved from the negative pole, and the whole apparatus was filled with carbonic anhydride. The tube containing the iron was heated to dull redness, and the current was passed through the hydrogen fluoride in the **U**-tube, which was cooled to — 50° by methyl chloride. In one experiment 0·130 gram of fluorine was absorbed by the iron, and 78 c.c. of hydrogen were liberated from the negative pole. No gas, except a small quantity of air, escaped from the tube containing the iron. The weight of iron fluoride formed is exactly equivalent to the quantity of hydrogen liberated at the negative electrode, and hence it follows that the gas evolved from the positive electrode is fluorine.

Fluorine can also be obtained by the electrolysis of fused hydrogen potassium fluoride. Under favourable conditions with liquid hydrogen fluoride 1·5—2 litres of fluorine can be obtained in an hour.

C. H. B.

Liquefaction and Solidification of Hydrogen Compounds. By K. Olszewski (*Monatsh. Chem.*, **7**, 371—374).—*Hydrofluoric acid* cooled to — 102·5° solidifies to a white, crystalline, transparent mass, becoming white and opaque at a lower temperature; on raising the temperature to — 92·3° the acid melts.

Hydrogen phosphide, PH_3, liquefies at — 90°, and solidifies at — 133·5 into a crystalline, semi-transparent mass; on raising the temperature it melts at — 132·5°, and boils about — 85°.

Hydrogen antimonide, SbH_3, prepared by collecting the first portions of gas evolved by adding dilute sulphuric acid to an alloy of 2 parts of antimony with 3 parts of zinc, solidifies at — 91·5°, but on raising the temperature to between — 65° and — 56° it partially decomposes with deposition of the antimony on the walls of the tube; this change is increased by raising the temperature to — 18°. This result explains the small proportion of hydrogen antimonide obtained in the various methods used for its preparation.

V. H. V.

Halogen Compounds of Sulphur. By W. Spring and A. Lecranier (*Bull. Soc. Chim.*, **45**, 867—873).—The compounds of sulphur with chlorine of the formulæ S_2Cl_2, S_3Cl_4, SCl_2, and the corresponding iodine and bromine compounds, were carefully prepared. The author then determined whether the halogen was actually combined with the sulphur in the proportions in which they were presented to one another, or whether these elements were partly present in the free state mixed with perhaps a certain proportion of a definite haloïd compound. To do this, a reaction was employed, in which the haloïd compounds of sulphur act on potassium sulphite, the potassium compound of the

haloïd, and tri-, tetra-, or penta-thionates are formed respectively; the presence, however, of any uncombined haloïd causes the formation of potassium sulphate in the proportion of 1 mol. of sulphuric acid for every molecular proportion of free haloïd present. The examination thus conducted indicates that these haloïd compounds do actually exist at the usual temperature, but always accompanied by a certain amount of the uncombined elements, which are, however, always in the exact ratio of the constituents of the definite compound with which they exist. The proportion of uncombined elements being apparently constant for each temperature, and representing the coefficient of dissociation for that temperature. The general results obtained are as follows:—

S_2Cl_2	contains	6·82	per cent.	of its	elements	in the free state.
S_3Cl_4	,,	8·45	,,	,,	,,	,,
SCl_2	,,	9·45	,,	,,	,,	,,
S_2Br_2	,,	27·11	,,	,,	,,	,,
S_3Br_4	,,	29·06	,,	,,	,,	,,
SBr_2	,,	38·40	,,	,,	,,	,,
S_2I_2	,,	90·12	,,	,,	,,	,,
S_3I_4	,,	88·89	,,	,,	,,	,,
SI_2	,,	89·97	,,	,,	,,	,,

A. P.

Note.—The above figures apparently refer to the normal temperature, and are merely comparative.

Formation of Sulphuric Acid in the Preparation of Dithionic Acid. By W. Spring and E. Bourgeois (*Bull. Soc. Chim.*, **46**, 151—156).—An aqueous solution of sulphurous acid consists of a mixture of sulphurous acid and water containing sulphurous anhydride in solution, the amounts of the free water and sulphurous anhydride varying with the temperature; on acting on such a solution with manganic dioxide, it unites with the sulphurous acid to form manganic dithionate, and with the sulphurous anhydride to form manganic sulphate, with an increase of temperature therefore more sulphuric and less dithionic acid is formed; the same is the case if the violence of the reaction is increased by employing the manganic peroxide in a more finely divided state, the temperature being thus indirectly raised. If therefore a solution of hydrogen sodium sulphite be employed in the place of a solution of sulphurous acid a larger amount of dithionic acid is formed. Ferric and nickelic oxides may be employed instead of manganic dioxide. A. P.

Reduction of Sulphurous Acid by Hydrogen Phosphide. By A. Cavazzi (*Gazzetta*, **16**, 169—172).—A solution of sulphurous acid in contact with an atmosphere of hydrogen phosphide is slowly deoxidised with precipitation of sulphur and formation of phosphoric acid, and traces of hypophosphorous acid. The final change may be expressed thus: $PH_3 + 2H_2SO_3 = H_3PO_4 + 2H_2O + S_2$, although it is probable that the reactions take place in three successive changes, leading to the production of hypophosphorous, phosphorous, and

finally phosphoric acid. In presence of mercury, the liberated sulphur combines at once with the metal to form the sulphide, thus: $PH_3 + H_2SO_3 + Hg = H_3PO_2 + H_2O + HgS$; the presence of hypophosphorous acid was confirmed by the production of cuprous hydride by the action of copper sulphate on the solution from which the excess of hydrogen phosphide had been boiled off. V. H. V.

Action of Hydrofluoric Acid on Silica and Silicates. By J. B. Mackintosh (*Chem. News*, **54**, 102).—The author's results indicate that "generally speaking those minerals which have a more condensed molecule are less easily attacked than those with a less condensed molecule." The treatment of quartz and opal is given as an example:—1 gram of each, reduced to a uniform average size of 0·003 cub. mm., were digested with dilute (9 per cent.) hydrofluoric acid for one hour in the cold, opal lost 77·28 per cent., quartz 1·56 per cent. With quartz crystals and pieces of opal of corresponding size the difference is still more marked. These differences are regarded as not merely chemical, but as connected with those molecular dissimilarities which give rise to the variations in crystalline form.

D. A. L.

Electrolysis of Aqueous Ammonia with Carbon Electrodes. By A. Millot (*Compt. rend.*, **103**, 153—155).—The alcoholic solution of the residue obtained by evaporating the black solution (Abstr., 1885, 1125) contains an azulmic substance, together with urea and the products of its decomposition, ammelide, biuret, and guanidine. No cyanuric acid is formed. These substances are not obtained if the solution electrolysed contains sodium chloride as in Bartoli and Papasogli's experiments, since they are destroyed by the nascent chlorine which is liberated under these conditions.

C. H. B.

Alcoholate of Potassium Hydroxide. By R. Engel (*Compt. rend.*, **103**, 155—157).—Potassium hydroxide was suspended in a platinum basket in alcohol until the latter was saturated. Under these conditions the liquid separates into two layers, the lower being an aqueous and the upper an alcoholic solution of potassium hydroxide. If the alcoholic solution is kept at 0° for 24 hours it deposits unctuous, white, crystalline plates which have the composition KHO + 2EtHO, and alter rapidly when exposed to air. This alcoholate of potassium hydroxide may be kept in closed vessels at 0° without undergoing alteration, but at 30° it gradually decomposes. At 60° the crystals melt, and after some hours the liquid separates into two layers; this decomposition is very rapid at 100—120°. The alcoholate decomposes in accordance with the equation $KHO,2EtHO = EtOK + EtOH + H_2O$. The liberated water is saturated with potassium hydroxide, and forms the lower layer of liquid. The upper alcoholic layer when cooled deposits slender needles which seem to have the composition EtOK + EtOH.

The formation of potassium ethoxide by the action of heat on alcoholic potash explains the action of the latter on certain organic compounds. C. H. B.

Alcoholate of Potassium Hydroxide. By E. J. Maumené (*Compt. rend.*, **103**, 215—216; compare preceding Abstract).—The author obtained a crystallised alcoholate of potassium hydroxide of the composition KHO + 2·44EtHO in 1872 (*Théorie Générale*). This compound gradually becomes converted into a crystallised colourless salt, $C_2H_7O_2K$, which gives characteristic reactions with several metallic salts. C. H. B.

Hydrated Sodium Sulphide. By C. Göttig (*J. pr. Chem.* [2], **34**, 229—237).—When a solution of soda in strong alcohol is saturated with hydrogen sulphide to a certain degree, the hydrate $Na_2S + 6H_2O$ is first formed, and then, after the solution has lost some of its water, the hydrates $2Na_2S + 11H_2O$ and $Na_2S + 5H_2O$. These all disappear after continued action of hydrogen sulphide. In presence of anhydrous alcohol, they give up part of their water of crystallisation, whilst when treated with weak alcohol they take up water and yield the hydrate $Na_2S + 9H_2O$. This addition of water is accompanied by a change of crystalline form.

By the action of hydrogen sulphide on a solution of caustic soda in weak alcohol, the hydrate $Na_2S + 6H_2O$ is first formed, owing to the heat evolved in the reaction, and then the hydrate with 9 mols. H_2O. N. H. M.

Explosive Mixture. By Cavazzi (*Gazzetta*, **16**, 172).—In the course of some experiments on the reduction of alkaline nitrates, it was observed that equal parts of sodium nitrate and hypophosphite form a powerfully detonating mixture. It is probable that the reaction is as follows: $NaH_2PO_2 + 2NaNO_3 = Na_3PO_4 + H_2O + NO_2 + NO$. V. H. V.

Silver Carbonate. By G. S. Johnson (*Chem. News*, **54**, 75).—Some silver hydroxide suspended in water and exposed to the air in a loosely covered vessel was found after two months to have deposited large, glistening, yellow, prismatic crystals of silver carbonate. These melt at a low red heat, and soon afterwards decompose rapidly with the evolution of abundance of gas. Silver carbonate precipitated from solutions by means of sodium carbonate is amorphous, but resembles the crystalline form in other properties. 1 litre of water saturated with carbonic anhydride at 15° dissolves 0·846 gram of pure precipitated silver carbonate, and when this solution is exposed to air for 12 hours, a yellow precipitate of crystalline silver carbonate separates. D. A. L.

Magnesia containing Rare Earths (?) By G. S. Johnson (*Chem. News*, **54**, 88).—A very thoroughly washed sample of calcined magnesia was observed to render water alkaline, the alkalinity disappearing after a time. The magnesia apparently contained two earths, one with a soluble the other with an insoluble sulphate, but both having their oxides and carbonates soluble, and their phosphates insoluble in alkaline solutions. D. A. L.

Didymium and Cerium Tungstates and Molybdates. By A. Cossa (*Gazzetta*, **16**, 284—288; comp. this vol., p. 772).—Amorphous cerium tungstate, fused with potassium chloride, is converted into a crystalline modification, isomorphous with scheelite, and consisting of dimetric octahedra (comp. Didier, this vol., p. 595). Under similar conditions didymium molybdate is obtained in octahedral crystals ($a:b:c = 1:1:1{\cdot}569$) of a rose-red colour and vitreous lustre; sp. gr. $= 4{\cdot}75$. Cerous molybdate is obtained isomorphous with wulfenite by heating the precipitated compound in an inert atmosphere, or by its slow precipitation from a mixture of aqueous solutions of cerous sulphate and sodium molybdate. The crystals obtained by heating this precipitate in a crucible at the temperature of molten nickel possess an axial ratio $a:b:c = 1:1:1{\cdot}558$, and sp. gr. $4{\cdot}56$. Amorphous lead molybdate may in like manner be converted into a crystalline modification. V. H. V.

Combination of Potassium Alum with Water. By E. J. Maumené (*Bull. Soc. Chim.*, **46**, 261—262).—Potassium alum was dried by keeping it in the presence of a large quantity of the same alum from which all water had been expelled, the temperature being maintained at the point at which the crystals of alum commenced to lose water, until the weight was constant. The alum thus prepared contained 49·99 per cent. of water and, therefore, has the formula $A(H_2O)_{28{\cdot}73}$, a result which agrees with the proportion of water indicated by the author's theory. (Compare this vol., p. 421.) A. P.

Fluosilicates of Aluminium and Glucinum. By C. Chabrié (*Bull. Soc. Chem.*, **46**, 284—285).—The fluosilicates of aluminium and glucinum described by Berzelius and Attenberg are amorphous compounds, but by the prolonged boiling of 0·5 gram of aluminium chloride or the recently precipitated hydrate, with 200 grams of the acid, a distinctly crystalline fluosilicate separates on cooling, which does not alter on drying at 100°. Aluminium fluoride treated by this method yields a similar compound. A. P.

Crystallised Basic Sulphates. By Athanasesco (*Compt. rend.*, **103**, 271—272).—The author has obtained several crystallised basic sulphates by heating the normal sulphates with water in sealed tubes, at temperatures varying from 150° to 275°. They are insoluble in, and not decomposed by water, and all except the mercury compound contain water, which they only lose at a somewhat high temperature.

If a 3 per cent. solution of zinc sulphate is heated at 200—250°, the compound $SO_4(ZnOH)_4$ is obtained in colourless, transparent needles, which seem to belong to the rhombic system. The analogous cadmium compound is obtained in a similar manner, and forms monoclinic or triclinic needles. A 25 per cent. solution of zinc sulphate, heated at 160° with a small quantity of the oxide, yields the compound $SO_3,4ZnO + 7H_2O$, which crystallises in very light, unctuous, hexagonal lamellæ.

When a 3 per cent. solution of normal aluminium sulphate is heated at 250°, the compound $4SO_3,3Al_2O_3,9H_2O$ is obtained in transparent

colourless rhombohedrons which closely resemble cubes. A 25 per cent. solution of ferric sulphate, heated at 150°, yields the analogous compound $4SO_3,3Fe_2O_3,9H_2O$ in pale yellow rhombohedrons. A 3 per cent. solution of ferric sulphate, heated at 275°, yields a brown crystalline powder, which seems to have the composition $SO_3,10Fe_2O_3,H_2O$, but may be a mixture.

A 3 per cent. solution of normal uranyl sulphate at 250° forms a citron-yellow, microcrystalline powder of the composition

$$SO_3,3U_2O_3,2H_2O;$$

a 15 per cent. solution at the same temperature yields greyish-yellow, microscopic needles of the compound $SO_3,4U_2O_3,7H_2O$.

In the cases of nickel and cobalt, 5 grams of the sulphate are boiled for 6—8 hours with 1—2 grams of the corresponding carbonate or barium carbonate, the liquid concentrated to 30—40 c.c., filtered whilst boiling, and the filtrate heated at 230—240° in the case of nickel, and at 200° in the case of cobalt. The products are respectively pale green, microscopic needles of the composition $5SO_3,6NiO,4H_2O$, and a bluish-green, crystalline powder of the composition

$$SO_3,6CoO,10H_2O.$$

To obtain similar compounds of mercury and bismuth, a solution of the nitrate in dilute nitric acid is heated at 250° with an excess of sodium sulphate. The mercury salt thus formed, $SO_3,4HgO$, crystallises in deep yellow, transparent rhombohedrons; the bismuth salt, $2SO_3,3Bi_2O_3,2H_2O$, forms white, microscopic needles. C. H. B.

Sodium Manganites. By G. Rousseau (*Compt. rend.*, **103**, 261—264).—When manganese chloride is fused in presence of air with potassium chloride containing some potassium hydroxide, a series of manganites is formed which will be subsequently described.

When 1 part of manganous chloride is fused in presence of air with a mixture of 10 parts of sodium chloride and 3 parts of sodium hydroxide, no manganite is formed, but crystals of the oxide Mn_3O_4 are obtained. The manganite is only produced when the proportion of sodium hydroxide exceeds that of the chloride, and even under these conditions the salt does not crystallise in the fused mixture.

If 3 grams of sodium hydroxide are fused in a platinum crucible, mixed with 1·5 gram of dry manganous chloride and 3 grams of sodium nitrate, heated to dull redness until the greater part of the nitrate is decomposed, then raised to the temperature at which the hydroxide volatilises, and kept at this temperature for about four hours, the residue after treatment with water yields black silky needles of the manganite $12MnO_2,Na_2O$. The presence of sodium chloride (formed by the action of the hydroxide on the manganous chloride) is essential to the formation of the manganite, for if the manganese chloride is replaced by the carbonate or peroxide no crystals of the manganite are obtained. Other manganites are formed if the conditions of the reaction are somewhat varied, and these are being investigated.

If the above mixture is heated in a Bunsen flame until all the

sodium hydroxide has volatilised, and is then mixed with 10 grams of dried sodium chloride, and heated to orange redness until all the chloride is volatilised, the manganite $5MnO_2,Na_2O$ is obtained in black, rhombohedral lamellæ.

If the mixture is heated to bright redness, and after volatilisation of the first 10 grams, a second quantity of 10 grams of sodium chloride is added, and the heating continued until this also is driven off, black needles of the manganite $12MnO_2,Na_2O$ are obtained, identical in all respects with those obtained by heating the first mixture with a Bunsen lamp.

At dull redness and bright redness, the manganite $12MnO_2,Na_2O$ is formed, whilst the compound $5MnO_2,Na_2O$ is the product at an intermediate temperature. In the case of barium and strontium, the simplest manganite is formed at both extremes of temperature, and the more complex compound at the mean temperature. The formation of these compounds shows that manganese peroxide is analogous to silicic anhydride, molybdic anhydride, &c., in its power of forming complex salts. C. H. B.

Compounds of Ammonia with Metallic Permanganates. By T. Klobb (*Compt. rend.*, **103**, 384—385).—If a solution of potassium permanganate is saturated with ammonia, and then mixed with a quantity of silver nitrate equivalent to the amount of permanganate, the compound $AgMnO_4,2NH_3$ is precipitated in the form of a crystalline powder, very slightly soluble in cold water, but more soluble in hot water. The powder consists of microscopic rhombic plates. It detonates when struck, and decomposes when heated, giving off ammonia and leaving an insoluble residue.

Salts of copper, cadmium, nickel, zinc, and magnesium under similar conditions yield similar compounds, which, however, have not yet been analysed.

Cobalt salts give a brown precipitate only, but if a concentrated solution of luteo-cobalt chloride (1 mol.) is mixed with potassium permanganate (6 mols.), a crystalline precipitate is formed, which can be recrystallised from boiling water. It forms cubes, octahedra, and cubo-octahedra of the composition $Co_2(MnO_4)_6,12NH_3$, which explode when heated or struck. In presence of excess of luteo-cobalt chloride, violet hexagonal lamellæ are formed which contain chlorine.

The ammonia in these compounds is not expelled by simply boiling with an alkaline hydrate, since under these conditions some nitrite is formed. The permanganate must first be reduced by means of sulphurous acid. C. H. B.

Chromium Oxyfluoride. By V. Oliveri (*Gazzetta*, **16**, 218—222).—The compound of chromium and fluorine, first isolated by Unverdorben, although prepared by a method analogous to that of chromium oxychloride, is generally considered to contain chromium and fluorine only in the atomic ratio of one to six. Further, the synthesis of carbon compounds containing fluorine has been explained on the supposition that the chromium perfluoride is reduced to a compound containing proportionally less fluorine (Abstr., 1885, 1224).

In order to ascertain how far these views are correct, the author has determined the atomic ratio of chromium to fluorine in the above-mentioned compound, and also studied its action on toluene. Firstly, the atomic ratio of the two elements was found to be as one to two, and secondly, with toluene it yields a compound, $PhMe[OCr{\cdot}OH]_2$, analogous to the compound obtained by Etard under similar conditions from the same hydrocarbon and chromium oxychloride, and like it, decomposed by water with formation of benzaldehyde (Abstr., 1881, 581). The compound therefore is CrO_2Fl_2. V. H. V.

Action of Hydrogen Peroxide on the Oxides of Chromium. By MARTINON (*Bull. Soc. Chim.*, **45**, 862—864).—When a solution of chromic acid is treated with an acid solution of hydrogen peroxide, the deepest blue coloration is obtained if the ratio of the hydrogen peroxide to chromic acid is as 4 : 2; perchromic acid, $Cr_2O_7H_4$, is therefore a product of the reaction; this compound is blue in the presence of acids; after a time, it is slowly decomposed into oxygen and chromium sesquioxide; in neutral or alkaline solutions, the colour of the perchromic acid changes to a dirty red, and the decomposition is more rapid, chromic acid or a chromate being formed. When chromium dioxide in an alkaline solution is treated with hydrogen peroxide, an alkaline chromate is formed, but no oxygen is evolved; in a neutral solution, the reaction takes place very slowly, a small amount of chromic acid being formed; in acid solutions, a salt of chromium sesquioxide is formed and oxygen evolved, the chromium dioxide acting exactly as a chromate of chromium sesquioxide, CrO_3,Cr_2O_3. Hydrogen peroxide has no action on chromium sesquioxide in neutral or acid solutions; in alkaline solutions a chromate is immediately formed. A. P.

Compound of Stannic Chloride with Hydrogen Chloride. By R. ENGEL (*Compt. rend.*, **103**, 213—215).—When a current of dry hydrogen chloride is passed for a long time over the hydrate $SnCl_4 + 5H_2O$, the latter becomes completely liquid, and when saturated with the gas at 28°, has the composition Cl 46·4; Sn 30·7; H_2O 22·9 = 100; sp. gr. at 28° = 1·971. When cooled to 0°, the liquid deposits crystalline leaflets of the composition $SnCl_4,2HCl + 6H_2O$, which melt at about 20°, and yield a liquid of sp. gr. 1·925 at 27—28°. If more strongly heated, the compound loses hydrogen chloride. The mother-liquor from the crystals has the composition Cl 46·3; Sn 31·24; H_2O 22·46; sp. gr. at 28° = 1·977. When again saturated with hydrogen chloride at 0°, it deposits more crystals of the same compound, the second mother-liquor having a sp. gr. 2·015.

The compound $SnCl_4,2HCl + 6H_2O$, called *chlorostannic acid* by the author, is analogous to chloroplatinic acid, $PtCl_4,2HCl + 6H_2O$; it is the acid corresponding with the well-known chlorostannates.

C. H. B.

Note by Abstractor.—The name chlorostannic acid has already been used by Mallet to denote a compound of the composition SnO_2HCl (Trans., 1879, p. 524).

Barium and Strontium Titanates. By L. Bourgeois (*Compt. rend.*, **103**, 141—144).—Equivalent quantities of titanic anhydride and barium carbonate were fused at a bright red heat for an hour with an excess of barium chloride, and the product extracted with very dilute hydrochloric acid. A residue was thus obtained consisting of yellow microscopic crystals with a brilliant lustre. These crystals are cubes or cubo-octahedra, which, with polarised light, show all the phenomena characteristic of pseudo-cubic crystals, and are found to consist of a complex aggregation of rhombic lamellæ. They have the composition $2BaO,3TiO_2$; sp. gr. = 5·91.

The corresponding strontium compound is obtained in a similar manner. It forms smaller greyish-yellow or pale-yellow cubes without modifications, and the bi-refractive power is very feeble, but in other respects its properties agree with those of the barium compound; sp. gr. 5·1.

Under similar conditions, calcium compounds yield crystals identical in composition and properties with perowskite, CaO,TiO_2.

The addition of sodium or potassium chloride to the fused mass has no appreciable effect. If silica is added as well as titanic oxide, barium compounds yield a crystalline scoria which is under investigation; the strontium crystals are modified by small octahedral faces, but calcium compounds yield perowskite without any trace of sphene. C. H. B.

Germanium. By C. Winkler (*J. pr. Chem.* [2], **34**, 177—229; compare this vol., pp. 421 and 774).—Germanium is obtained by heating finely powdered argyrodite with calcined sodium carbonate and flowers of sulphur at a moderate red heat. The product is extracted with water, and the solution treated with the exact amount of sulphuric acid necessary to decompose the whole of the sodium sulphide present. After being left for a day, the solution is separated from the precipitate consisting of sulphur, and arsenic and antimony sulphides, and treated with hydrochloric acid so long as a precipitate is formed. The whole is then saturated with hydrogen sulphide, filtered, and the white voluminous precipitate of germanium sulphide washed with 90 per cent. alcohol saturated with hydrogen sulphide. The sulphide is roasted at a low temperature, warmed with strong nitric acid, and the oxide so obtained ignited; it is then reduced.

Germanium melts at about 900°, and volatilises at a temperature slightly above its melting point. On cooling, it crystallises in octahedra. It is very brittle, and can be readily powdered. It has a metallic lustre, and is whiter than zirconium. Sp. gr. = 5·469 at 20·4°. When a drop of the fused metal is allowed to fall on to paper, it divides itself into several globules, which move continually over the surface of the paper. The metal is converted by nitric acid into a white oxide; it is soluble in sulphuric, but not in hydrochloric acid. The atomic weight of germanium is 72·32; the number 72·28 was obtained from measurements of the wave-lengths of the most brilliant lines of the spectrum. Determinations of the specific heat of germanium made by Nilson and Petterson, at temperatures from 100 to 440°,

point to the number 0·0758; the atomic heat is 5·48. The specific heat of germanium dioxide is 0·1293.

Germanious oxide, GeO, is obtained by boiling germanious chloride with caustic potash; a *hydroxide*, probably $Ge(OH)_2$, is first formed, and this is converted into the oxide by heating it in a current of carbonic anhydride. It forms a greyish-black powder, readily soluble in hydrochloric acid; the solution so obtained yields a yellow precipitate when treated with alkali, and white and reddish-brown precipitates with potassium ferrocyanide and with hydrogen sulphide respectively. It reduces permanganates to manganates, and precipitates gold and mercury from solutions of their salts.

Germanium dioxide (germanic acid ?), GeO_2, is formed when germanium is burned in oxygen, and may be obtained in the pure state by decomposing the chloride with water. It is a dense white gritty powder; sp. gr. = 4·703 at 18°. It dissolves in 247·1 parts of water at 20°, and in 95·3 parts at 100°, and separates in microscopic rhombic or rhombohedric crystals. The aqueous solution has an acid taste. It dissolves readily in alkaline hydroxides and carbonates when fused with them.

Germanious sulphide, GeS, is obtained in splendid thin plates by heating the disulphide in a slow current of hydrogen. The crystals are greyish-black, and have an almost metallic lustre, but are quite transparent, and are red in transmitted light. When heated in presence of air, it is converted into the dioxide. It dissolves readily in warm potash, leaving a residue of metallic germanium as a microscopic crystalline powder. When the solution is treated with hydrogen sulphide, the sulphide separates as a reddish-brown amorphous precipitate.

Germanium disulphide, GeS_2, is best prepared by precipitating a solution of the dioxide with hydrogen sulphide in presence of much free mineral acid, and washing the white precipitate so obtained with alcohol saturated with hydrogen sulphide; it is then washed with ether, and dried in a vacuum. If the sulphide is washed with water until free from acid, and then put into water, it yields an emulsion which requires several weeks to become clear; the liquid appears then to contain the sulphide in a colloïdal state, and after repeated filtration contained 1 part in 221·9 parts of water. The solution in water decomposes quickly, with evolution of hydrogen sulphide. The disulphide dissolves readily in alkaline hydrosulphides, probably with formation of sulpho-salts.

Germanious chloride, $GeCl_2$ (?), is obtained by passing hydrogen chloride over heated germanium or its sulphide. It forms a colourless thin liquid, boiling at about 72°. The low boiling point indicates the possibility of the substance being a compound, $GeHCl_3$, corresponding with silicium chloroform, the compound not yet having been analysed.

Germanic chloride, $GeCl_4$, is prepared by the direct combination of germanium and chlorine; the product of the reaction is shaken with mercury and distilled. It may also be prepared by heating germanium with eight times its weight of dry mercuric chloride. It forms a thin, colourless liquid boiling at 86°; sp. gr. = 1·887 at 18°. When exposed to air, it fumes considerably, but less than the dichloride. Water decomposes it with formation of an oxide; the reaction gives rise to

considerable development of heat. When a mixture of germanium chloride with hydrogen is passed through a red-hot tube, germanium is deposited on the wall of the tube; the reduction is, however, only partial.

Germanic iodide, GeI_4, is best prepared by heating germanium in a current of carbonic anhydride containing iodine vapour. The reaction takes place with much less ease than in the case of the chloride, and the product always contains free iodine, even when an excess of the metal is present. It is an orange-coloured substance, which melts at 144°, and boils between 350° and 400°; the vapour is yellow, and is inflammable; when mixed with air and ignited it detonates feebly. It is very hygroscopic. In determining the vapour-density, it was found that it does not dissociate at 440°, but does considerably at 658°.

Germanium is most readily identified by the formation of the white sulphide when its alkaline solution is treated with ammonium sulphide, and subsequently with a large excess of hydrochloric acid. The quantitative estimation is also carried out by means of the sulphide, which is then converted into the oxide.

The atomic weight and the properties of germanium show that it is identical with Mendeléeff's ekasilicon, occupying the position between gallium and arsenic in the periodic arrangement of the elements (compare *Annalen*, Suppl. **8**, 200). N. H. M.

Platinum Salts. By E. Prost (*Bull. Soc. Chim.*, **46**, 156—160). —On evaporating a solution of platinic hydroxide dissolved in concentrated nitric acid, a reddish salt, $Pt(NO_3)_2,3PtO_2,5H_2O$, insoluble in water, is formed, and on adding water to the original solution, the hydrate, $PtO_2,3H_2O$, is formed as a yellow precipitate; this on filtration yields a filtrate, the further addition of water to which causes the formation of the hydrate $Pt_3O_4,9H_2O$; and lastly, on adding water to the original nitric acid solution and then boiling, a precipitate having the composition $Pt_5O_{11},11H_2O$ is obtained, which is, however, probably a mixture of hydrates.

When a solution of platinic hydrate in perchloric acid is evaporated in a vacuum, it yields a red basic compound, insoluble in water, and having the composition $Pt_6ClO_9,15H_2O$.

An acid solution of platinic sulphate, absolutely free from nitric acid, after standing for several days, yields an abundant brick-red precipitate, having the composition $PtSO_4(OH)_2,4Pt(OH)_4,3H_2O$, the liquid becoming almost colourless; if, however, the solution of the sulphate is boiled, a precipitate having the composition $Pt_8SO_4O_{13},16H_2O$, is formed.

Double sulphates of platinum and the alkali-metals were prepared by mixing cold concentrated aqueous solutions of the alkaline and platinic sulphates, the latter being in excess; they are all pulverulent brown substances, the ammonium and rubidium compounds being soluble in water, whilst those of potassium are insoluble. The salts prepared were: $2(NH_4)_2SO_4,Pt_8(SO_4)_3 + 25H_2O$; $Pt_6Rb_6(SO_4)_4 + 17H_2O$; $3K_2SO_4,Pt_{10}O_{10}(SO_4)_2 + 34H_2O$; $5K_2SO_4Pt_{18}O_{22}SO_4 + 34H_2O$. A. P.

Mineralogical Chemistry.

Crystallisation of Gold. By E. S. Dana (*Amer. J. Sci.*, **32**, 132—138).—The delicate crystalline and arborescent forms of the gold from the White Bull Mine, in Oregon, appear on examination to be made up of acute rhombohedral forms, closely crowded on each other. The terminal crystal usually shows the presence of a six-sided pyramid at the apex. In rare cases, three other minute planes are observed, forming an obtuse termination to the hexagonal pyramid. Measurements show that the planes observed are all those of 303, and that the apparent rhombohedral symmetry is due to the fact that the crystals are uniformly elongated in the direction of the octahedral axis.

The author also describes a specimen of gold from Tuolumne Co., California, in the Yale collection. It consists of a series of octahedra in parallel position, passing from the small solid crystals to larger ones with cavernous faces, and their edges in ridges, and to others looking as if they were made of bent wire. In addition to the large octahedral faces, there are those of 303, usually strongly striated, a hex-octahedron ($18O\frac{9}{5}$), one set of whose edges are truncated by 303, and traces of a second hex-octahedron (402). B. H. B.

Embolite. By C. Welch (*Chem. News*, **54**, 94—95; 162).—With regard to the composition of embolite (compare this vol., p. 430), the author remarks that it may be a single mineral with rather large variation in composition, but is much more likely an indefinite mixture of hornsilver and bromite. In support of this, he quotes in detail 14 analyses from various well-known authorities, dating from 1844 to the present year; of these one supports the formula AgCl,AgBr; four the formula 3AgCl,2AgBr; two require 5AgCl,2AgBr, whilst of the remaining seven each suggests a separate formula, and, moreover, the amount of silver chloride varies from about 20 to 82 per cent.

D. A. L.

Cornish Tinstones and Tin-Capels. By J. H. Collins (*Jahrb. f. Min.*, 1886, ii, Ref., 184—185; *Min. Mag.*, **5**, 121—130).

The author gives a list of the minerals which are associated with cassiterite in the different kinds of country rock in Cornwall. He distinguishes those which appear to have been formed contemporaneously with the cassiterite, and those which have been observed in immediate contact with it, and mostly deposited upon it.

The constant occurrence of gilbertite in the granitic veins of tin oxide in Cornwall, renders its composition a matter of importance. The author, therefore, gives three analyses; Nos. 1 and 2 were from Stenna Gwynn, and No. 4 from St. Just.

	SiO_2.	Al_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.
I.	45·10	36·00	1·10	trace	1·50	0·90	11·40
II.	44·90	35·80	0·70	trace	1·60	0·50	10·40
III.	48·12	34·90	0·65	trace	0·31	0·22	9·71

	Li_2O.	F.	H_2O.	Total.
I.	trace	0·54	3·70	100·24
II.	trace	0·72	4·21	98·83
III.	trace	1·42	3·21	98·54

Of Cornish tourmaline two analyses are given; I, a radiated black variety from the kaolin of Little Carclaze, and II, from the Trevisco kaolin. The results were as follows:—

	SiO_2.	Al_2O_3.	$Fe_2O_3 + FeO$.	MnO.	MgO.	CaO.	Alkalis.
I.	46·12	18·40	21·90	—	0·50	0·40	4·50
II.	43·22	23·14	20·87	0·10	0·40	0·51	4·44

	B_2O_3.	Loss on ignition.	F.	Total.
I.	5·40	1·50	0·68	99·40
II.	5·60	1·47	0·25	100·00

B. H. B.

Brookite from Magnet Cove, Arkansas. By S. L. Penfield (*Amer. J. Sci.*, **31**, 387—389).—The author describes a crystal of brookite, of unusual form, from Magnet Cove, in the collection of Professor G. J. Brush, and figures and describes some of the forms which are common at the locality. The crystals are frequently loose, or are attached to quartz. They vary in size up to 2 cm. in diameter. The forms observed are: $\breve{P}2$, $\frac{1}{2}\breve{P}$, $\frac{1}{2}\breve{P}2$, $\infty\breve{P}\infty$, P, and $2\breve{P}\infty$.

B. H. B.

Calamine. By A. B. Griffiths and S. Dreyfus (*Chem. News*, **54**, 67).—The specimen examined occurs in the south-west of Siberia, associated with barium sulphate and galena in a matrix of limestone. It is found in right-rhombic prisms belonging to the prismatic system; hardness between 5 and 6; sp. gr. 4·629. The percentage composition of the crystals is:—Zn 50·03, Fe 2·77, Cd 0·92, Mn 0·12, SiO 5·62, CO_2 35·21, water 5·33. Calamine when found crystalline has hitherto been in the form of rhombohedrons, so that it would appear to be dimorphous, and isodimorphous with calcite and aragonite.

D. A. L.

Composition of Herderite and Beryl. By S. L. Penfield and D. N. Harper (*Amer. J. Sci.*, **32**, 107—117).—The crystals of herderite examined were carefully picked by hand, crushed, and suspended in the Thoulet solution; the material of sp. gr. greater than 2·95 alone being used for analysis. Over 5 grams of very pure material were thus obtained. Analysis gave—

P_2O_5.	BeO.	CaO.	F.	H_2O.	Total.	Less O.	Total.
43·74	15·51	33·67	5·27	3·70	101·89	2·22	99·67

Herderite is, therefore, an isomorphous mixture of $CaBeFPO_4$ with $CaBe(OH)PO_4$, which may be written $CaBe(FOH)PO_4$. Chemically, herderite is closely related to wagnerite, triplite, and triploidite, three minerals offering a good illustration of the isomorphism of F and OH, and the authors are of opinion that in herderite there is another strong proof of this interesting relation.

S. L. Penfield has published (Abstr., 1885, 490) a series of analyses showing that alkalis are sometimes present in beryl to a large extent, and that water is always given off by ignition. The ammonium carbonate method employed in the determination of berylia, the authors find, gives too low results, and these analyses are only of value as showing to what extent alkalis and water are present. In order to renew the investigation, some very pure beryl (aquamarine from Stoneham, Maine) was selected, and analysed as carefully as possible by Genth's method, the results being as follows:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	BeO.	CaO.	Na_2O.	Li_2O.
65·54	17·75	0·21	0·38	13·75	0·06	0·71	trace

H_2O.	Total.	Sp. gr.
2·01	100·39	2·706

Regarding the water as essential, the authors add $\frac{1}{2}H_2O$ to the ordinary accepted formula of beryl, or write it $H_2Be_6Al_4Si_{12}O_{27}$.

B. H. B.

Actinolite Rock from Dalecarlia. By A. B. Meyer (*Jahrb. f. Min.*, 1886, ii, Mem., 255—257).—A rock from the Ryllshytte Company Mine, described as an amphibole rock resembling nephrite, gave on analysis the following results:—

SiO_2.	FeO.	MnO.	Al_2O_3.	CaO.	MgO.	Loss on ignition.	Total.	Sp. gr.
57·50	4·05	0·13	2·00	13·09	20·77	0·66	98·20	3·023

The rock is much softer than true nephrite. The sp. gr. is comparatively high, and the percentage of water is another point of difference, true nephrite always containing about 2 per cent. of water. The results of the microscopic examination clearly show that the rock is not nephrite, but an actinolite rock mineralogically resembling nephrite.

B. H. B.

A New Type of Pyroxene. By R. de Chroustschoff (*Jahrb. f. Min.*, 1886, ii, 345).—In the basalts of Rossberg, light-green crystals of augite occur, exhibiting the forms: $\infty P\bar{\infty}$, $\infty P\breve{\infty}$, ∞P, $P\bar{\infty}$, and more rarely $\infty P2$, $\infty P\bar{2}$, P. The crystals are quite transparent and free from inclusions. The extinction along $\infty P\breve{\infty}$ is on an average 39°. Analysis gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Na_2O.	K_2O.	Total.
49·18	2·15	4·96	9·04	20·30	13·07	1·89	0·30	100·89

B. H. B.

Ptilolite, a New Mineral. By W. Cross and L. G. Eakins (*Amer. J. Sci.*, **32**, 117—121).—This mineral occurs in cavities of an augite-andesite in the conglomerate beds of Green and Table Mountains, Colorado. It occurs in most delicate, white tufts, and spongy masses composed of short, hair-like needles, loosely grouped together. Examined under the microscope, these needles are found to be colourless, transparent prisms, the average diameter of which is less than

0·001 mm. An analysis of 0·5 gram of pure material gave the following results:—

SiO_2.	Al_2O_3.	CaO.	K_2O.	Na_2O.	H_2O.	Total.
70·35	11·90	3·87	2·83	0·77	10·18	99·90

The authors propose to name this mineral *ptilolite*, from πτίλον, *down*. The substance belongs to the alumino-silicates of which no previously described hydrate contains so high a percentage of silica.

B. H. B.

Specimens of Mica from the Rheinwaldhorn, Graubünden. By E. A. Wülfing (*Ber.*, **19**, 2433—2438).—In this paper, analyses are given of two specimens of mica from the Rheinwaldhorn in the Graubünden canton, and the results obtained are compared with those calculated by Tschermak's theory. The results are as follows:—

	TiO_2.	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.
Specimen 1....	0·11	47·69	28·3	1·02	3·88	2·72
„ 2....	0·18	47·72	25·96	1·76	6·55	2·30

	K_2O.	Na_2O.	H_2O.	Sp. gr.
Specimen 1....	9·06	1·87	4·07	2·86
„ 2....	10·18	1·70	3·42	2·89

The first specimen was of a greyish-green tint, which at ordinary temperatures appeared to be uniaxial, but, on warming, its true diaxial character was revealed; the second specimen was of a rather darker tint, markedly diaxial and pleochroitic. Both may be classed with phengite.

V. H. V.

Topaz and Garnet in Rhyolite. By W. Cross (*Amer. J. Sci.*, **31**, 432—438).—The author has described the occurrence of topaz in the rhyolite of Chalk Mountain, Colorado. He now describes a second occurrence of topaz in rhyolite at Nathrop, Colorado. The rhyolite contains numerous more or less rounded cavities, called by v. Richthofen *lithophyses*. The outer walls of these are formed of a pure white mineral, which is seldom developed in recognisable form. A microscopic examination shows the mineral to be sanidine. Quartz crystals and ore particles are occasionally met with. Garnet occurs in isolated crystals of 2·5 mm. in diameter, of a dark-red colour, clear and transparent. In chemical composition, this garnet proves to be a typical spessartite, analysis having given the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	K_2O.	Na_2O.
35·66	18·55	0·32	14·25	29·48	1·15	0·27	0·21

H_2O.	Total.	Sp. gr.
0·44	100·33	4·23

The crystals of topaz are prismatic, clear and transparent, or pale-blue or yellow.

This is, it is believed, the first known occurrence of garnet in cavities of rhyolite. The mode of formation of the topaz and garnet is not fully determinable, but it is evident that they are not secondary products but primary, and produced by sublimation or crystallisation from presumably heated solutions, contemporaneous with the final consolidation of the rock.

The only rhyolites known to contain topaz in the manner described agree quite remarkably in composition. They are all silica-alumina-alkali rocks; other constituents being present in almost insignificant quantities. B. H. B.

Pseudomorphs of Limonite after Iron Pyrites. By E. G. Smith (*Amer. J. Sci.*, **31**, 376—377).—The pseudomorphs occur in limestone, at Carpenter's Quarry, near Beloit, Wisconsin. All stages of metamorphism are represented. An analysis of a nodule weighing 26 grams gave the following results:—

SiO_2.	S.	FeO.	Fe_2O_3.	CaO.	MgO.	Loss on ignition.	Total.	Sp. gr.
6·25	0·31	0·91	80·21	0·04	0·40	11·72	99·84	3·45

The metamorphism is therefore quite complete. B. H. B.

Crystallographic Association of Triclinic Felspars. By R. Breon (*Compt. rend.*, **103**, 170—172).—Some labradorites from Krakatoa contain microliths which have the optical properties of labradorite, whilst some of the large crystals behave like labradorite and others like anorthite. In the majority of cases, however, the crystals are in aggregations, parts of which show the extinctions of labradorite, whilst other parts show the extinctions of anorthite. Many of the crystals, twinned in the manner of albite, have a concentric structure, and examination by Lévy's method shows that each of the crystals is a mixture of the two triclinic felspars. In order to verify this result, thin sections of the mineral were heated at 80° with strong hydrochloric acid for 2 to 6 hours, washed with water, and placed in a solution of magenta. The colouring matter is absorbed by the gelatinised portions, but does not affect the unattacked minerals. The delicacy of the test is increased if the magenta solution is allowed to evaporate slowly on the thin layer of mineral before washing away the excess. Under these conditions, it is found that the microliths are quite unattacked, some of the large crystals are unaltered, whilst others are completely decomposed, and a large number of crystals show a completely decomposed nucleus, which retains the form of the crystals and is surrounded by an unaltered external zone with the properties of labradorite, the separation between the altered and unaltered portions being perfectly sharp and distinct. If the action of the acid is prolonged, the labradorite is slightly attacked. It is worthy of note that the twinned crystals do not consist of alternate plates of labradorite and anorthite. The association of the two felspars has not taken place by twinning, but by the superposition of concentric zones, the anorthite having crystallised first and afterwards become enveloped in a crystalline crust

of labradorite. This is a case of mechanical isomorphism, very different from chemical isomorphism as defined by Mitscherlich.

C. H. B.

Anorthite Rocks from St. Thomas (Antilles). By J. v. Siemiradzki (*Jahrb. f. Min.*, 1886, ii, Mem., 175—180).—A small series of specimens of crystalline rocks from the Island of St. Thomas have been examined in the Mineralogical Laboratory of the University of Warsaw. The series consists of three rocks, in which the felspar constituent is anorthite. The principal rock in the island is a highly altered corsite (I), rich in secondary opal. Near the town of St. Thomas, the rocks analysed under Nos. II and III occur as veins in the corsite. Both are highly altered, so that it is difficult to form an opinion of their original constitution. Analyses of the three rocks gave the following results:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	H_2O.	CO_2.	K_2O.	Na_2O.
I.	53·46	13·35	—	16·74	10·94	3·07	1·64	0·80	—	—
II.	71·17	13·16	—	6·54	4·31	1·87	2·95	—	—	—
III.	45·31	9·96	3·43	12·99	16·44	2·56	3·77	5·39	0·25	0·41

B. H. B.

Volcanic Rocks of Assab. By L. Ricciardi (*Gazzetta*, **16**, 209—212).—In this paper analyses are given of three specimens of lava from Assab, an African province at present occupied by Italy. The specific gravities of the three samples were 2·703, 2·401, and 2·331, and the analysis of the first, which does not differ materially from the others, gave the following results:—

SiO_2.	P_2O_5.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	Cr_2O.	CaO.
46·67	0·74	12·64	6·13	10·07	0·19	0·34	11·48

MgO.	K_2O.	Na_2O.	Loss on ignition.
3·64	2·31	1·64	2·64

In chemical composition this lava resembles those of Iceland and Armenia, and in specific gravity that of Vesuvius, although it differs from the latter in containing less alumina and potash, but more iron. It differs also from the lava of Etna in its lower sp. gr. and in containing less silica, alumina, and soda, but more iron. It resembles, however, certain basalt rocks of Sicily. V. H. V.

Peridotite of Elliot Co., Kentucky. By J. S. Diller (*Amer. J. Sci.*, **32**, 121—125).—Several years ago two dykes of an interesting eruptive rock were discovered seven miles south-west of Willard, Kentucky. Examination under the microscope shows the rock to belong to the peridotites. The peridotite is a compact, dark-green rock, with a specific gravity of 2·781. The approximate percentage mineralogical composition is as follows:—

Primary minerals: Olivine, 40; pyrope, 8; biotite, 1; enstatite, 1; ilmenite, 2·2; apatite, trace.

Secondary minerals: Serpentine, 30·7; dolomite, 14; magnetite, 2; octahedrite, 1·1.

Analysis gave the results given in the following table:—

	1.	2.	3.	4.	5.
H_2O at 110°	0·14	0·17	0·20	8·92	0·51
H_2O at red heat	0·66	—	—	—	—
CO_2	—	—	—	6·66	—
SiO_2	40·05	41·32	0·76	29·81	60·56
TiO_2	0·07	0·16	49·32	2·20	1·19
P_2O_5	0·04	none	trace	0·35	0·30
Cr_2O_3	0·24	0·91	0·74	0·43	—
Al_2O_3	0·39	21·21	2·84	2·01	16·19
Fe_2O_3	2·36	4·21	9·13	5·16	5·19
FeO	7·14	7·93	27·81	4·35	2·41
MnO	0·20	0·34	0·20	0·23	0·36
NiO	—	—	—	0·05	—
CaO	1·16	4·94	0·23	7·69	2·09
MgO	48·68	19·32	8·68	32·41	1·30
K_2O	0·21	0·07	0·19	0·20	4·82
Na_2O	0·08			0·11	4·78
SO_3	—	—	—	0·28	—
Totals	101·42*	100·58	100·10	100·86	99·70
Sp. gr.	3·37	3·67	4·45	2·78	2·63

	6.	7.	8.	9.
H_2O at 110°	0·85	1·94	—	1·40
H_2O at red heat	2·32	5·17	8·78	9·00
CO_2	6·29	—	0·55	0·88
SiO_2	60·78	60·25	41·32	35·53
TiO_2	0·03	0·23	0·48	0·95
P_2O_5	0·09	0·10	0·08	0·08
Cr_2O_3	—	—	trace	—
Al_2O_3	10·54	23·18	20·71	18·23
Fe_2O_3	3·27	1·53	2·59	2·46
FeO	—	3·42	5·46	4·81
MnO	0·10	0·10	0·17	0·13
NiO	—	—	—	—
CaO	10·15	0·51	9·91	21·17
MgO	1·59	3·52	1·91	2·01
K_2O	2·36	3·17	0·88	1·08
Na_2O	1·41	0·39	7·19	2·53
SO_3	—	—	—	—
Totals	99·78	103·51†	100·03	100·26
Sp. gr.	—	—	—	2·48

1, Olivine; 3, pyrope; 3, ilmenite; 4, peridotite; 5, a fragment of syenite, found upon the border of the peridotite, and supposed to have been brought up from a great depth; 6, calcareous sandstone near dyke; 7, fine-grained fissile sandstone near dyke; 9, fragment of

* 99·42 in original. † 100·51 in original.

slate included in the peridotite. The peridotite is clearly a truly eruptive rock, which traverses many thousand feet of Palæozoic strata to reach the surface. B. H. B.

Weathering of Granite. By A. Hilger and K. Lampert (*Landw. Versuchs-Stat.*, 1886, 161—169).—Louisenberg granite, when weathered to a slight extent only, forms fairly compact masses, which are readily broken by a blow, the interior portion of the mass consisting apparently of ferric oxide, together with slightly weathered felspar. Besides being subjected to chemical analysis, the granite was also subjected to microscopical examination. The method of analysis, as well as the analytical data, are fully given. The results show that the weathering was normal, and that the original stone, which consisted of oligoclase, mica, and quartz, had by reason of the action of the carbonic anhydride and oxygen, lost the oxide Me″O, including FeO in the form of $Me''(HO)_2(CO_3)_2$. The silica passing into the hydrated condition, and therefore having become soluble, the products intermediate between kaolin and granite are richer in the sesquioxides, whilst the monoxides have decreased. These facts, together with others, are quite in accordance with other results obtained by the investigators. E. W. P.

Granitic Rocks of the Ural. By A. Arzruni (*Jahrb. f. Min.*, 1886, ii, Ref., 367—368).—The finely granular muscovite granite, termed by G. Rose *beresite*, traverses the chlorite- and talc-schists of Berjósowsk.* The composition of the rock is as follows:—

SiO_2.	Al_2O_3.	CaO.	MgO.	K_2O.	FeS_2.	H_2O.	Total.
64·41	23·67	0·68	0·32	(5·97)	2·23	2·72	100·00

This corresponds with—

Quartz.	Mica.	Iron pyrites.
34·82	62·95	2·23

In this case, as in many other apparently quite unaltered rocks, the felspar has been completely removed. B. H. B.

Two Masses of Meteoric Iron of Unusual Interest. By W. E. Hidden (*Amer. J. Sci.*, **31**, 460—465).—The first of these meteorites was found in June, 1884, on a mountain seven miles east of Batesville, Independence Co., Arkansas. It weighs 94 lbs., and belongs to the class "Holosiderite" of Brezina, being free from stony matter, and closely resembling the irons of Chulafinnee (Abstr., 1881, 394), Alabama, and Whitfield Co. (Abstr., 1882, 153). It is 17 inches long and 8 inches thick. Its most interesting feature is the presence of a hole through it, near the edge, measuring five-eighths of an inch in diameter at its smallest part, and cone-shaped from both sides. An analysis of a piece cut from the edge gave the following results:—

Fe.	P.	Ni and Co.	Total.
91·22	0·16	(8·62)	100·00

* This spelling is, according to the author, more correct than the usual "Beresowsk."

The second mass of meteoric iron was found in 1857 in the north-western corner of Laurens Co., South Carolina. It is cuboidal in shape, and its weight is 4 lbs. 11 oz. The perfection of the Widmannstätten lines, as shown in the smoothed surface, is unusual. The analytical results place this mass among the few that are exceedingly rich in nickel and cobalt. Its cobalt percentage is above that of any other on record. Analysis gave—

Fe.	Ni.	Co.	P.	S.	Total.
85·33	13·34	0·87	0·16	trace	99·70

B. H. B.

Thermal Springs of Hammam Salahine. By J. Girard (*J. Pharm.* [5], **13**, 264—266).—These two springs are found in the midst of extensive ruins at the place named, on the left bank of the Oued Mellèque, 20 kilos. from Kef, and 420 metres above sea-level. Gypsum abounds all around, and the springs appear at the base of hills of this mineral. On 28th July, 1884, the external temperature being 28°, the temperature of the water was 40·8° and 40·2° respectively; the results of the analyses were as follows:—I. Reaction alkaline, alkalinity equivalent to 0·38 gram sulphuric acid. Solid residue 8·810 grams per litre. Cl 4·440; SO_3 0·369; CO_2 0·402; SiO_2 0·026; CaO 0·412; MgO 0·143; Na 2·826. Bromides and iodides absent. II. Alkaline reaction. The water became turbid in contact with air and on boiling; Fe 0·231 gram per litre. This iron was probably in the state of carbonate. The waters are much employed both for bathing and drinking by the Arabs; and, judging from the extensive ruins, were appreciated by the Romans. J. T.

Analysis of the Hot Springs of Leuk. By G. Lunge and R. E. Schmidt (*Zeit. anal. Chem.*, **25**, 309—314).—The St. Lorenz spring yields about half a million litres in 24 hours. The water has a temperature of 51·35°; specific gravity at 15° = 1·00194 compared with water at 15°, or 1·00109 compared with water at 4°. It is clear and inodorous, and has a flattish taste. On exposure to the air, it deposits traces of ferric hydrate.

The gas, which is regularly evolved in large bubbles from the spring, has the following composition in volumes per cent.:—

CO_2.	O.	N.
2·12	traces	97·88

The results of two concordant analyses of the dissolved matters are given, and from them the following composition is calculated:—

	Grams per kilogram.
Strontium sulphate	0·00194
Calcium sulphate	1·42866
Magnesium sulphate	0·26912
Sodium sulphate	0·08715
Calcium carbonate	0·09650
Magnesium carbonate	0·02066

	Grams per kilogram.
Ferrous carbonate	0·00011
Manganous carbonate	0·00024
Sodium chloride	0·00121
Potassium chloride	0·01127
Lithium chloride	0·00037
Ammonium chloride	0·00017
Alumina	0·00051
Silica	0·03020
Copper carbonate	minute trace
Barium sulphate	trace
Calcium phosphate	,,
Calcium fluoride	,,
Arsenic	,,
Nitric acid	,,
Carbonic anhydride	1·97 c.c. = 0·00390
Oxygen	0·66 ,, = 0·00094
Nitrogen	7·21 ,, = 0·00905

Details are given of the methods of analysis in so far as they differ from those in general use. M. J. S.

Waters at Bagnères de Luchon, Haute Garonne. By E. Willm (*Compt. rend.*, **103**, 416—418). The results are given in grams per litre:—

	Bayen.	Reine.	Bosquet.	Pré No. 1.
Sulphur, as sulphides	0·0313	0·0223	0·0241	0·0309
Thiosulphuric acid, S_2O_3	0·0026	0·0040	0·0013	0·0032
Sulphuric acid, SO_4	0·0092	0·0353	0·0257	0·0117
Carbonic acid, CO_3	0·0264	0·0240	0·0360	0·0237
Chlorine	0·0553	0·0469	0·0474	0·0585
Silica	0·0933	0·0670	0·0796	0·0899
Ferric oxide	0·0021	0·0031	0·0009	0·0010
Alumina	—	—	0·0003	—
Sodium	0·0975	0·0810	0·0934	0·0986
Potassium	0·0041	0·0036	0·0049	0·0074
Calcium	0·0045	0·0107	0·0082	0·0043
Magnesium	0·0005	0·0015	0·0019	traces
Total solids	0·3268	0·2994	0·3237	0·3292
Carbonic anhydride, total	0·0523	0·0462	0·0615	0·0600
Temperature	64·5°	57·5°	44°	62°

The high proportion of silica is especially noteworthy. Traces of iodine, lithium, copper, ammonia, manganese, phosphoric acid, and notably boric acid, are also present. Arsenic is absent.

C. H. B.

Mineral Waters of Warmbrunn in Silesia. By T. Poleck (*Jahrb. f. Min.*, 1886, ii, Ref., 364—365).—The author gives the results of analyses of two hot springs, bored in 1882 in the granite at a depth of 25 and 167 metres respectively, the temperatures being

24·5° and 26° respectively, and the sp. gr. 1·00047. Unlike the other Warmbrunn springs formerly analysed, they contain no organic substances and no sulphuretted hydrogen. The spring gases consist of pure nitrogen, carbonic anhydride and combustible gases being absent.

The results of the analyses, in grams per litre, are as follows :—

Sodium chloride	0·070877	0·067520
,, bromide	0·000221	0·000221
,, iodide	0·000027	0·000027
Potassium sulphate	0·010529	0·010590
Sodium sulphate	0·223758	0·222836
,, carbonate	0·120600	0·133785
Lithium carbonate	0·000872	0·000846
Calcium ,,	0·022455	0·022571
Magnesium carbonate	0·000567	0·000860
Ferric oxide	0·000750	—
Silica	0·086250	0·088435
Totals	0·536906	0·547691*

Traces of nickel, antimony, arsenic, phosphoric, and boric acids, and fluorine were observed. B. H. B.

Organic Chemistry.

Higher Normal Paraffins, C_nH_{2n+2}. By F. Krafft (*Ber.*, **19**, 2218—2223).—*Decyl iodide*, $C_{10}H_{21}I$, is prepared by passing hydrogen iodide through decyl alcohol and subsequently heating the product moderately in a water-bath. It is then left for some time, washed with water and with very dilute caustic soda solution, and distilled. It boils at 132° under 15 mm. pressure, sp. gr. 1·2768 (water at 4° = 1). Sodium converts it into didecyl (normal icosane).

Normal primary nonyl alcohol, $C_9H_{20}O$, is readily obtained by distilling barium nonylate with barium formate under reduced pressure, and reducing the distillate with glacial acetic acid and zinc-dust; the acetate so formed is saponified with alcoholic potash. The alcohol melts at − 5°, boils at 107·5° under 15 mm. pressure, and at 213·5° under 760 mm. pressure. Sp. gr., $d_0 = 0·8415$; $d_{10} = 0·8346$; $d_{20} = 0·8279$ (water at 4° = 1). *Nonyl iodide* boils at 117°; sp. gr. $d_0 = 1·3052$; $d_{16} = 1·2874$; when treated with sodium it is converted into dinonyl (normal octadecane).

Dioctyl (normal hexadecane) was prepared by the action of sodium on octyl iodide; it melts at 18·2—18·3°, and boils at 157·5° under 15 mm. pressure; sp. gr., $d_{18·2} = 0·7754$.

Diheptyl was prepared from normal heptyl iodide and found to be

* 0·434979 in original.

identical with tetradecane from myristic acid; it melts at 5·4—5·5°. The author considers the best method for preparing the higher normal paraffins to be the action of sodium on the normal primary iodides; the result is, however, not so good when a mixture of iodides is used. N. H. M.

Nitro-compounds of the Fatty Series. By P. Alexéeff (*Bull. Soc. Chim.*, **46**, 266—268).—The author discusses the various formulæ proposed for the so-called nitroethane obtained by V. Meyer, and considers it to be isonitrosoethyl alcohol, OH·CMe : N·OH, this view of its constitution best explaining its decomposition by hydrochloric acid into acetic acid and hydroxylamine, and also many other of its characteristic reactions. A. P.

Action of Aluminium Bromide on Ethylene and on the Bromides of the Alcohols, C_nH_{2n+1}·OH. By G. Gustavson (*J. pr. Chem.* [2], **34**, 161—177).—When dry ethylene and hydrogen bromide are passed over aluminium bromide, a liquid product is obtained, together with a gas consisting of paraffins. A current of dry carbonic anhydride is passed through the liquid to remove free hydrogen bromide, ethylene and ethyl bromide. The compound was found on analysis to have the formula $AlBr_3,C_4H_8$. It is an orange-coloured liquid, insoluble in light petroleum and carbon bisulphide, miscible with methyl bromide. Water decomposes it with formation of liquid unsaturated hydrocarbons, boiling at 150 to 300°. An analogous compound, $AlCl_3,C_4H_8$, was obtained from aluminium chloride in a similar manner. The compound $AlBr_3,C_4H_8$ is also obtained by heating aluminium bromide (1 mol.) and ethyl bromide (4 mols.) at 60—70°. When treated with ethylene and hydrogen bromide at 0°, a gas is obtained consisting of hydrocarbons, C_nH_{2n+2}, with some unchanged ethylene.

Ethyl bromide, primary and secondary propyl bromides, and isobutyl bromide all react with these compounds of hydrocarbons and aluminium bromide. In the case of the reaction with ethyl bromide, the resulting hydrocarbon-aluminium bromide has nearly the same composition as the original compound, whilst in the other reactions compounds are formed containing larger organic radicles; the amount of gas evolved (consisting of hydrocarbons C_nH_{2n+2}) also increases with the molecular weight of the bromide employed.

Methyl bromide reacts with hydrocarbon aluminium bromide, yielding, not as was expected, a product containing less organic radicle, but more; the methyl having replaced hydrogen. A compound containing less hydrocarbon than is represented in the formula $AlBr_3,C_4H_x$ could not be obtained. N. H. M.

Preparation of Chloroform. By G. Michaelis and W. T. Mayer (*Dingl. polyt. J.*, **261**, 496).—When a crude acetate, for instance calcium acetate, is subjected to destructive distillation only a small quantity of acetone, $COMe_2$, boiling at 56°, is produced, whilst comparatively large quantities of dimethylacetal, $C_2H_4(OMe)_2$, boiling between 60° and 65°, ethylmethylacetal, $C_2H_4(OEt)$·OMe, boiling at 85°, methyl ethyl ketone, COMeEt, boiling between 75° and 80°, diethyl

ketone, $COEt_2$, boiling between 75° and 80°, and metacetone, $C_6H_{10}O$, boiling between 82° and 86° are formed, besides other still higher-boiling ketones, together with a large quantity of oil containing ketones. Pure sodium acetate yields essentially acetone in addition to a small quantity of these higher-boiling substances. Whilst, however, pure acetone gives only about 30 per cent. of chloroform when distilled with hypochlorites, the above-named substances yield a much larger percentage. The process of preparing the chloroform consists in subjecting crude acetates to dry distillation at temperatures varying between 300° and 500°, treating the products with hypochlorites, condensing the chloroform therefrom by distillation, and purifying by rectification. D. B.

Action of Light on Iodoform. By G. Daccomo (*Gazzetta*, **16**, 247—251).—It has long been known that iodoform in solution when exposed to direct sunlight is decomposed with evolution of iodine. In this paper quantitative determinations are quoted to show that all the iodine is thus eliminated. It is further proved that the presence of oxygen is necessary for this change, which consists in an oxidation of the carbon, and may in all probability be represented by the following equation $2CHI_3 + 5O = 3I_2 + 2CO_2 + H_2O$.

V. H. V.

Ethenyl Trisulphide. By J. Bongartz (*Ber.*, **19**, 2182—2184).—*Ethenyl trisulphide*, CMe : S_3 : CMe, is obtained by treating thiacetic acid with fused zinc chloride; hydrogen sulphide is slowly evolved, and in 12 hours the whole becomes almost solid. The product is washed with water containing hydrochloric acid, boiled with potash, and crystallised from alcohol. It is a colourless crystalline, substance, readily soluble in ether and chloroform, more sparingly soluble in alcohol, and insoluble in water. It melts at 224—225°, above which temperature it sublimes in slender needles. Potassium hydroxide and hydrosulphide at 200° to 220° act on it but slightly.

N. H. M.

Preparation of Trichloromethylsulphonic Chloride. By H. Bassett (*Chem. News*, **54**, 79—80).—100 grams of powdered potassium chlorate, 200 c.c. of hydrochloric acid, 400 c.c. of water, and 50 c.c. of carbon bisulphide are mixed in a flask and left loosely covered, exposed to light. Action soon commences with evolution of gas, &c.; in direct sunlight it may become too violent and require cooling, therefore in summer it is best to use more water, and in winter less (equal volumes of acid and water). The mixture is agitated from time to time until the evolution of gas ceases and the carbon bisulphide has become solid, which may be in a few days in summer, or a fortnight in winter; the slow reaction is best for a good yield; as much as 43 grams of trichloromethylsulphonic chloride have been obtained from 50 c.c. of carbon bisulphide. The white solid is separated from the acid, washed, well pressed, dried over sulphuric acid, and sublimed. D. A. L.

Reduction of Carbonic Anhydride by Potassium Cyanide. By A. Eiloart (*Chem. News*, **54**, 88).—When potassium cyanide is heated in a current of dry carbonic anhydride, it blackens, fuses,

turns white, and increases in weight, carbonic oxide being formed, as shown in the equation $KCy + CO_2 = KCyO + CO$. The blackening of the cyanide is due to exposure to the air, for if it is cooled and then re-heated without exposure to the air, no blackening occurs.

D. A. L.

The Cyanuric Radicle and its Compounds with Halogens. By P. Klason (*J. pr. Chem.* [2], **34**, 152—160).—Cyanuric chloride is conveniently prepared in the following way: 85 grams of dry hydrogen cyanide are passed into 325 grams of chloroform kept cool by means of ice and salt; dry chlorine is then passed in for some time after the solution has acquired a yellow colour. The whole is allowed to remain for 12 hours, after which it is boiled with a reflux condenser until the hydrogen chloride, the excess of chlorine and the unchanged cyanic chloride are removed. The chloroform and cyanuric chloride are readily separated from each other by distillation. The yield varied from 80 to 130 grams. About 50 grams of hydrocyanic acid hydrochloride are also formed. The author considers that the polymerisation is caused by the excess of chlorine. Hydrogen chloride appears to act in a similar way but to a smaller extent.

Cyanuric chloride is not decomposed by water containing hydrochloric acid (compare Naumann and Voigt, *Ber.*, **3**, 523). When cyanuric chloride is boiled with methyl or ethyl alcohol, or with phenol, cyanuric acid and an alkyl chloride are formed.

When cyanuric iodide is heated to 360°, it gives off iodine and yields paracyanogen. From this it is concluded that paracyanogen has at least 6 carbon-atoms, and that it has the same relation to cyanuric compounds as free cyanogen has to cyanides. The formula of paracyanogen would thus be $(CN)_3 : (CN)_3$.

Monochlorocyanuric iodide, $(CN)_3ClI_2$, is obtained as a white, feathery sublimate by heating cyanuric iodide (containing chloride) at 360°. Water decomposes it at 125° into cyanuric, hydrochloric, and hydriodic acids.

N. H. M.

Haloïd Derivatives of Acetonitrile. By L. Henry (*Compt. rend.*, **103**, 413—416).—*Iodacetonitrile*, obtained by the action of the chlorine-derivative on an alcoholic solution of sodium iodide, is a colourless liquid which becomes brown when exposed to light, and is insoluble in water, but readily soluble in alcohol and ether. It is highly corrosive, has a pungent odour which excites weeping, and boils at 186—187° with slight liberation of iodine, and towards the end of the operation hydrocyanic acid and iodine are liberated; sp. gr. at 12° = 2·3065. It decomposes slowly in contact with air, and acts readily on silver salts; with silver acetate acetoxyacetonitrile is produced.

Bromacetonitrile is obtained by the regulated action of bromine-water on the iodine-derivative, twice the theoretical quantity of bromine being used. The free iodine and bromine are removed by careful treatment with alkalis, and the product is extracted with ether. Bromacetonitrile closely resembles the iodine-derivative in its properties, and boils at 148—150° under ordinary pressure without decomposition; sp. gr. at 12° = 1·7710; vapour-density, 4·06.

The irritant and corrosive action of haloïd-derivatives of nitriles increases with the atomic weight of the halogen. The proximity of the nitrogen increases the aptitude of the halogens to react with positive elements. The extent to which the influence of the proximity of the nitrogen is exerted depends on the other atoms in the molecule. It is most marked when the nitrogen and the halogen are united with the same carbon-atom, as in cyanogen chloride; it is well marked when they are separately united to two carbon-atoms which are in direct union, as in acetonitrile; but it disappears altogether when the carbon-atoms to which the nitrogen and the halogen are respectively united are separated by a CH_2-group, as in the derivatives of propionitrile. C. H. B.

Action of Chlorine on Potassium Seleniocyanate. By A. Verneuil (*Compt. rend.*, **103**, 144—146).—When a current of air mixed with a small proportion of chlorine is passed over the surface of a 10 per cent. solution of an alkaline seleniocyanate, the red crystalline precipitate which first forms, gradually changes to a yellow substance which may be dried and purified by crystallisation from chloroform. It forms golden-yellow plates of the composition $C_2N_2Se_3$, which are slowly decomposed by cold water, and rapidly by boiling water, into hydrocyanic acid, selenious acid, and selenium, $2C_2N_2Se_3 + 2H_2O = 4HCN + SeO_2 + Se_5$; but the greater part of the selenium is due to the action of the selenious acid on the seleniocyanic acid which is at first liberated, for in presence of calcium carbonate the action takes place in accordance with the equation $2C_2N_2Se_3 + 3CaCO_3 = 2Ca(CNSe)_2 + CaSeO_3 + Se + 3CO_2$. The compound $C_2N_2Se_3$ may therefore be regarded as a seleniocyanate in which the metal has been replaced by selenium.

When heated at 108° in a vacuum, selenium seleniocyanate yields a crystalline sublimate of selenium cyanide, $Se_2C_2N_2$, which is rapidly decomposed by boiling water into hydrocyanic acid, selenious acid, and selenium, but with cold water it yields selenium seleniocyanate, ammonium cyanide, ammonium seleniocyanate, and hydrocyanic acid, with selenious acid and carbonic anhydride.

The dark red compound formed by the first action of chlorine is a compound of 1 mol. of selenium seleniocyanate with 1 mol. of potassium seleniocyanate and 1 mol. of water, $KSe(CNSe)_3 + H_2O$, and can be readily obtained by mixing a solution of selenium seleniocyanate in chloroform with the requisite quantity of a solution of potassium seleniocyanate in alcohol of 90°. The alcoholic solution of the double seleniocyanate decomposes somewhat rapidly with precipitation of selenium. On evaporation, it yields the compound $C_3N_3KSe_3$. The corresponding ammonium compound, $Se(CN)_2,Se(CNSe)_2,2NH_4CNSe$, is obtained by boiling selenium seleniocyanate with moist ether for several hours.

The main action of chlorine on potassium seleniocyanate is expressed by the equation $16KCNSe + 7Cl_2 + 3H_2O = 5Se_3C_2N_2 + K_2SeO_3 + 6HCN + 14KCl$. C. H. B.

Decomposition of the Vapour of Ethyl Ether by Means of the Induction Spark. By N. v. KLOBUKOFF (*J. pr. Chem.* [2], **34**, 124—131).—When the vapour of ethyl ether is passed through a tube and subjected to the action of sparks from a Ruhmkorff's coil, only a slow decomposition takes place without separation of carbon. The spark is very brilliant, and has a strong violet colour. If the tube through which the ether vapour is passed is heated at 250—300°, decomposition takes place at once accompanied by an abundant separation of carbon. The chief products are hydrogen, carbonic oxide, ethylene, acetylene, and methane, and the homologues of the three last compounds. Water, carbonic anhydride or aldehydic substances could not be detected amongst the products of the decomposition.

In a similar manner, carbon bisulphide is decomposed into its constituents, the carbon separating near the points as a mirror with an almost metallic lustre. The sulphur separates as a white dust insoluble in carbon bisulphide. N. H. M.

Conversion of Glucoses into Dextrins. By E. GRIMAUX and L. LEFÈVRE (*Compt. rend.*, **103**, 146—149).—Pure glucose was dissolved in eight times its weight of hydrochloric acid of sp. gr. 1·026, the solution distilled in a vacuum on the water-bath, and the syrupy amber-coloured residue dissolved in water and precipitated by alcohol, solution and precipitation being repeated several times. The product was then dissolved in water, decolorised by animal charcoal, the solution concentrated by evaporation in a vacuum on the water-bath, and then allowed to evaporate in a vacuum at the ordinary temperature. The product thus obtained is a white powder which resembles ordinary white dextrin, is very hygroscopic, and forms gummy solutions. Its reducing and rotatory power vary with the number of times the substance has been redissolved and reprecipitated. When prepared by the method just described, the dextrin contains a small proportion of fermentable sugar, which can be removed by treatment with yeast. After purification in this way, one product had a reducing power of 17·8 per cent., whilst its rotatory power for $[\alpha]_D = + 97·48$.

The dextrin obtained in this way has the composition $3C_6H_{10}O_5 + H_2O$, and belongs to the class of achroodextrins. Its general properties resemble those of the dextrin obtained by Musculus by the action of sulphuric acid on glucose in presence of alcohol, but it has a lower rotatory and reducing power. It is not coloured by iodine, is unaffected by infusion of malt, and undergoes hydration somewhat slowly when boiled with dilute acids. The glucose formed from it by the action of acids is readily fermentable.

The alcoholic liquid from which the dextrin has been precipitated contains other dextrins with higher reducing powers, together with a fermentable sugar which is found by Fischer's reaction with phenylhydrazine and sodium acetate to be a mixture of glucose and maltose.

Galactose from milk-sugar behaves like dextrose, and yields a galactodextrin which resembles glucodextrin. Its reducing power in terms of glucose is 10 per cent., and its rotatory power for $[\alpha]_D = + 80$. C. H. B.

Corrosion of Boilers by Solutions of Sugar. By D. KLEIN and A. BERG (*Bull. Soc. Chim.*, **45**, 864—866).—The authors have investigated the frequent complaints made as to the action of sugar on boilers. By heating solutions of cane-sugar, invert-sugar, malt infusion, glycerol, and mannitol, in sealed tubes with a strip of boiler plate at 115° to 125° for about 70 hours, and estimating the amount of iron dissolved, they find that cane-sugar, invert-sugar, and malt infusion have a similar action, and dissolve a considerable amount of iron as acetate, hydrogen being given off and a caramel-like substance formed, the sugar solution having an acid reaction. Glycerol and mannitol have no action. Zinc, lead, and cadmium are also acted on by the sugar and malt solutions, the sugar being partially converted into the caramel-like substance. Copper, tin, and aluminium are not acted on, and although the solution becomes acid, no darkening takes place. A. P.

Substitution of Amidogen by Means of Sodamide. By J. WALTER (*J. pr. Chem.* [2], **34**, 132—133).—Ethylamine can be obtained by heating sodamide until it begins to melt in a current of dry hydrogen which has been passed through slightly warmed ethyl bromide; the product is passed into hydrochloric acid. (Compare Jackson and Wing, this vol., p. 623.) N. H. M.

Normal Propylamines. By C. VINCENT (*Compt. rend.*, **103**, 208—211).—Propyl iodide was heated in sealed tubes with 1·5 parts of alcoholic ammonia as in Hofmann's reaction, the product evaporated and distilled with potassium hydroxide, and the mixture of propylamines thus obtained was fractionated. The fraction boiling below 78° contained almost all the monopropylamine, whilst the second fraction boiling between 78° and 156° contained the di- and triamines.

The first fraction was mixed with alcohol and ethyl oxalate, heated, and then allowed to cool, when it deposited large prismatic needles of dipropyloxamide; this melts at 161·5°, and is insoluble in water, but may be purified by crystallisation from alcohol. The purified dipropyloxamide, when distilled with alcoholic potash, yields a mixture of alcohol and propylamine, from which the latter can be separated by conversion into chloride and redistillation, the hydrochloride being afterwards distilled with potash. *Propylamine* carefully dried over baryta boils at 49° under a pressure of 758 mm. The liquid from which the dipropyloxamide was separated is treated with potash, and yields a mixture of propylamines which is worked up with the crude product from a subsequent operation.

The fraction boiling at 78° to 156° was mixed with water, saturated with hydrochloric acid, concentrated by evaporation, and heated with its own weight of sodium nitrite. A reaction at once takes place with evolution of nitric oxide, together with some nitrogen and propylene derived from the monamine. The product is distilled in a vacuum, and yields an aqueous distillate with a supernatant yellow oily layer of nitrosodipropylamine mixed with tripropylamine. The oily liquid is carefully neutralised with pure dilute sulphuric acid,

and again distilled, when nitrosodipropylamine comes over and tripropylamine sulphate is left.

Nitrosodipropylamine, NPr_2NO, is a pale yellow liquid with an aromatic odour resembling that of hay; it boils at 205·9° under a pressure of 758 mm.; sp. gr. at 0° = 0·931. It is almost insoluble in water, but dissolves immediately in hydrochloric acid, with development of heat and formation of dipropylamine hydrochloride, oxychlorides of nitrogen being evolved. The reaction is complete after some days, when the hydrochloride may be decomposed by means of potash, and the amine dried over baryta. Pure *dipropylamine* boils at 97·5° under a pressure of 757 mm.; sp. gr. at 0° = 0·756. It has a strong odour of ammonia, burns with a luminous flame, and is slightly soluble in water, but the solubility decreases with rise of temperature. The amine dissolves a small quantity of water, which can be completely removed by means of baryta.

Tripropylamine, obtained from the sulphate, boils at 156·4° under a pressure of 757 mm., has a faintly ammoniacal odour, is almost insoluble in water, and burns with a very luminous flame; sp. gr. at 0° = 0·771. C. H. B.

Reactions of an Aqueous Solution of Dipropylamine with Metallic Salts. By C. Vincent (*Bull. Soc. Chim.*, **46**, 287—288).—With an aqueous solution of dipropylamine, salts of magnesium, glucinum, aluminium, zirconium, zinc, cadmium, tin, antimony, bismuth and lead all yield white precipitates insoluble in excess of the amine. Ferric salts yield an ochreous, nickel and chromium green precipitates, cobalt and copper blue, uranium, mercury, and gold yellow, whilst manganese forms a white precipitate which becomes coloured on exposure to the air. A. P.

Methylthialdine. By W. Markwald (*Ber.*, **19**, 2378—2382).—Thioaldehyde reacts with methylamine as with ammonia to form a methylthialdine, $C_7H_{15}NS_2$ (comp. this vol., p. 865). This substance crystallises in long needles, melting at 79°, insoluble in water, readily soluble in hot alcohol or ether. With acids, it forms very soluble salts, of which the hydrochloride crystallises in minute needles, and the thiocyanate in rhombic prisms. On boiling its aqueous solution, the latter is decomposed into γ-trithioaldehyde and dithioaldehyde isothiocyanate.

Methylthialdine may also be obtained by adding a slight excess of a concentrated solution of methylamine to a 10 per cent. aqueous solution of aldehyde, and passing hydrogen sulphide through the mixture. A slight variation of the conditions causes the experiment to be unsuccessful. The formation of methylthialdine by this process seems to be contradictory to the observations of Hofmann, who obtained by treatment of thialdine with methyl iodide, the hydriodide of a quaternary base, $C_7H_{15}NS_2,HI$. Accordingly Hofmann's experiments were repeated, and it is shown that thialdine yields with methyl iodide, thialdine hydriodide, together with methylthialdine methiodide: thus, $2C_6H_{13}NS_2 + 2MeI = C_6H_{13}NS_2I + C_7H_{15}NS_2MeI$. A mixture in equimolecular proportions of these two substances would

have the same percentage composition as Hofmann's supposed compound. This result also shows that methylthialdine is a tertiary, whilst thialdine is a secondary base, and that the most probable formula for the latter is $NH<^{CHMeS}_{CHMeS}>CHMe$, proposed by Erlenmeyer and others. V. H. V.

Conversion of Amides into Amines. By H. Baubigny (*Compt. rend.*, **103**, 149—151).—A claim (on behalf of the author and of Calm) for priority in the discovery of the conversion of amides into amines by the action of alcohols. (Comp. Seifert, Abstr., 1885, 963; and see Abstr., 1882, 972, and 1883, 175.) C. H. B.

Formaldehyde. By B. Tollens (*Ber.*, **19**, 2133—2136).—Referring to Loew's recent work on this subject (this vol., p. 609), the author finds still better results are obtained if the methyl alcohol, through which the air is passed, is warmed. Modifying the apparatus previously described (Abstr., 1882, 1277, and 1884, 293) by substituting for the platinum coil a coil of copper gauze, omitting the condenser and maintaining a constant stream of air, the author is able to obtain a 30—40 per cent. solution of formaldehyde with ease when the temperature of the bath is maintained at 45° to 50°. About 30 per cent. of the methyl alcohol is converted into formaldehyde, and over 700 grams of alcohol may be thus oxidised daily.

The author is now, in conjunction with C. Wehmer, investigating the substance named formose by Loew (*loc. cit.*). L. T. T.

Iodaldehyde. By P. Chautard (*Chem. News*, **54**, 87—88), and by W. P. Bloxam and E. F. Herroun (*ibid.*, 133).—In reply to a recent communication of the latter authors (this vol., p. 864), Chautard recognises the identity of his iodaldehyde with the substance obtained by them from an alcoholic solution of iodine by the action of nitric acid. He attributes their failure in applying his method (*ibid.*, 330) to working at too low a temperature (he worked at an average of 30—40°) and with too small quantities of material. This would explain both the slowness of the reaction and the non-isolation of iodaldehyde in their experiments, inasmuch as this substance is partially decomposed by prolonged contact with water, and the little that escapes decomposition would remain dissolved in the water. The author has obtained iodaldehyde by the action of iodine on aldehyde-ammonia, and has extended his work successfully to other aldehydes of the fatty series. Bloxam and Herroun state that they worked at a temperature of only 25°; they quite agree with Chautard in regarding Schoonbroodt's iodal as simply a mixture of iodoform and potassium iodide. D. A. L.

Action of Chlorine on Crotonaldehyde. By S. Zeisel (*Monatsh. Chem.*, **7**, 359—370).—In continuation of experiments on the synthesis of butyric chloral from α-monochlorocrotonaldehyde and α-crotonaldehyde (Abstr., 1883, 963), the action of chlorine on the aldehyde itself is studied. The action takes place in two stages;

at first a molecule of chlorine is taken up to form α-β-dichlorobutaldehyde, and at a higher temperature the chlorine replaces the hydrogen to yield α-β-dichlorobutyryl chloride, thus :—

$$CHMeCl\cdot CHCl\cdot CHO + Cl_2 = CHMeCl\cdot CHCl\cdot COCl + HCl.$$

That the compound thus obtained is not a trichlorobutaldehyde, the formation of which would be more probable *à priori*, is shown by the production of α-β-dichlorobutyric acid by the action of water and alkalis, and also of its methyl salt. The *α-β-dichlorobutyryl chloride* is a colourless liquid, boiling at 163·3—164·3° under 747 mm. pressure, of penetrating odour ; the corresponding *acid* forms acicular crystals melting at 57—59°, and boils at 132—133° under 27 mm. pressure. On the gradual addition of water to it, a clear liquid is at first produced ; then the addition of each successive drop causes a turbidity which disappears on agitation. Its *silver* salt is a white precipitate, and the *barium* salt a white, gummy mass. The properties of this acid mentioned above do not agree with those of the α-β-dichlorobutyric acid obtained by Friedrich from crotonic acid and chlorine (Abstr., 1883, 968). On distillation, it yields a mixture of two monochlorocrotonic acids. Its *methyl* salt is an oil of pleasant odour, which boils at 82·7—85·7° under an pressure of 28 mm., and at 174—180° under ordinary pressure, but under these conditions it is partially decomposed with evolution of hydrochloric acid. V. H. V.

Volatile Fatty Acids present in Commercial Lupuline. By J. Ossipoff (*J. pr. Chem.* [2], **34**, 238—240).—Analyses of barium salts are given prepared from fractions (boiling at 100—175°) of acids obtained by distilling lupuline with steam. N. H. M.

Propionic Acid. By A. Renard (*Compt. rend.*, **103**, 157—159).—Propionic acid was obtained in considerable proportion from the products of the destructive distillation of colophony at bright redness, and was carefully purified and dried. It boils at 141·5—142° under a pressure of 755 mm., remains liquid at 50°, and is soluble in all proportions in water, ethyl alcohol, ether, benzene, and light petroleum ; sp. gr. compared with water at 4° = 1·0089 at 0°, and 0·9904 at 18°.

An aqueous solution of propionic acid boils at 98·6—99·5°, and the composition of the distillate varies with the proportion of acid in the original solution. When the solution contains at least 40 per cent. of the acid, it boils at 99·5°, and the distillate contains 30 per cent. of acid, but towards the end of the operation the thermometer rises rapidly to 141—142°, at which temperature pure propionic acid distils over. The addition of calcium chloride causes propionic acid to separate from its solution, but sodium chloride and sodium sulphate have not this effect. The sodium salts, however, cause the acid to separate if the solution contains small quantities of butyric or valeric acid, benzene, or light petroleum. Acetic acid, on the other hand, tends to prevent the separation of propionic acid in this way.

C. H. B.

γ-Amidovaleric Acid. By T. Tafel (*Ber.*, **19**, 2414—2415).—By reducing the phenylhydrazine-derivative of levulinic acid with sodium amalgam, *γ-amidovaleric acid*, $NH_2 \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot COOH$, is produced; the yield is nearly theoretical. The acid, purified by means of its lead salt, crystallises in white leaflets melting at 193°, very soluble in water, insoluble in alcohol, ether and petroleum. Its *hydrochloride* forms a crystalline mass. The acid when heated at 250—260° is converted into an *anhydride*, C_5H_9NO, which forms colourless crystals and is very deliquescent, soluble in alcohol, ether, and benzene; with nitrous acid, it yields a nitroso-derivative, and on distillation with zinc-dust, an oil giving the pyrroline reaction, and probably containing its methyl-derivative. V. H. V.

Electrolysis of Normal Caproic Acid with Alternate Currents. By E. Drechsel (*J. pr. Chem.* [2], **34**, 135—151).—A solution of 200 grams of magnesium caproate in 3 litres of water, saturated with magnesium carbonate, was electrolysed with a Siemens and Halske's alternate current machine for 80 hours. Carbonic anhydride and hydrogen are evolved, but no oxygen or hydrocarbons; no oil is formed as in the case when the solution is subjected to ordinary electrolysis. The product was treated with sulphuric acid, separated from unchanged caproic acid, and distilled with steam. Valeric and butyric acids were found in the distillate, whilst the residue yielded oxalic, adipic, hydroxycaproic, and glutamic acids. Other acids are formed, but in quantities too small for identification. When magnesium caproate is electrolysed in the usual way, an oil having a strong odour is obtained, but no lower fatty acids or bibasic acids are formed. The author discusses the different effects produced by the different methods of electrolysis. It is suggested that the combustion of foods and tissues in the organism takes place in the same way, and follows the same laws as in the above experiments. N. H. M.

Glycidic Acids. By P. Melikoff (*Annalen*, **234**, 197—233).—Most of the author's results of his investigations on α- and β-methyl glycidic acids and on the action of hypochlorous acid on the isomeric crotonic acids, have already been published (Abstr., 1883, 969; 1884, 1301; 1885, 650). From these results, he arrives at the following conclusions. Although the glycidic acids are saturated compounds they possess the property of forming additive compounds with water, ammonia, and hydrochloric and hydrobromic acids. The energy of hydration decreases as the molecular weight increases. The power of hydration differs in different isomeric acids; it depends on their constitution. It is greatest in those acids in which oxygen is attached to a tertiary carbon-atom. Hydrochloric and hydrobromic acids combine as readily with the higher as with the lower members of the series. The elements of ammonia unite with glycidic acids, forming amidohydroxy-acids.

Hypochlorous acid unites with tiglic acid, yielding a mixture of *α-methyl-α-chloro-β-hydroxybutyric acid*, $OH \cdot CHMe \cdot CClMe \cdot COOH$, and *α-methyl-β-chloro-α-hydroxybutyric acid*, $CHMeCl \cdot CMe(OH) \cdot COOH$. The former acid melts at 111·5° and dissolves freely in alcohol and

water. The zinc, calcium, and barium salts are gummy masses, very soluble in water. α-Methyl-β-chloro-α-hydroxybutyric acid melts at 75° and dissolves freely in all solvents. The zinc salt is sparingly soluble in water. It crystallises in microscopic prisms or plates. The calcium salt is crystalline. Each of these acids is decomposed by alcoholic potassium hydroxide, forming *oxytiglic* or *$\alpha\beta$-dimethylglycidic acid*, $O\begin{cases}CH\cdot Me\\ |\\ CMe\cdot COOH\end{cases}$.

Potassium oxytiglate, $C_5H_7KO_3 + \frac{1}{2}H_2O$, crystallises in plates. It is soluble in hot alcohol and in water. The salt in hot aqueous solution slowly takes up water, forming potassium *$\alpha\beta$-dimethylglycerate*, $C_5H_9KO_4$. *Silver oxytiglate* crystallises in microscopic, rhombic plates. The hot aqueous solution deposits a metallic mirror. The barium and calcium salts are amorphous. The free acid is deposited from ether in silky needles. It melts at 62° and is soluble in water, alcohol, and ether. It unites with hydrochloric acid, forming α-methyl-β-chloro-α-hydroxybutyric acid melting at 75°, and with water forming *$\alpha\beta$-dimethylglyceric acid*. This substance crystallises in transparent prisms, melts at 107°, and dissolves in water, alcohol, and ether. It forms a crystalline potassium and a gelatinous silver salt. W. C. W.

Polymerisation of Propargylic Acid. By A. Baeyer (*Ber.*, **19**, 2185—2186).—The mother-liquor obtained in the preparation of propargylic acid from malic acid was found to contain trimesic acid. The same compound is formed in small quantities when propargylic acid is exposed for some time to sunlight, air being excluded. This polymerisatin of propargylic acid is analogous to the formation of benzene and tribromobenzene from acetylene and bromacetylene respectively. N. H. M.

Lactates. By H. Meyer (*Ber.*, **19**, 2454—2456).—*Barium lactate* with 2 or 1 mol. H_2O crystallises in rectangular needles, soluble in water and glycerol, insoluble in alcohol; the last molecule of water of crystallisation is not removed without decomposition. *Aluminium lactate* crystallises in anhydrous triclinic octahedra; *sodium aluminium lactate*, $Al_2(C_3H_5O_3)_3,(C_3H_4NaO_3)_3 + OH_2$, crystallises in rectangular prisms or tables. V. H. V.

Correction. By H. Weil (*Annalen*, **234**, 127—128).—Amidotrimethylbutyllactic acid, described by the author in a previous communication (this vol., p. 528), is identical with Heintz's amidotrimethylhydroxybutyric acid (this Journal, 1877, ii, 878). W. C. W.

Ethyl Acetoacetate and its Derivatives. By A. Isbert (*Annalen*, **234**, 160—196).—Ethyl acetoacetate is decomposed by sodium ethoxide (free from alcohol), yielding alcohol, ethyl acetate and the sodium salts of carbonic, acetic, and resacetic acids.

When sodium alkyl oxide acts on ethyl acetoacetate in presence of an alcohol, the chief product is the ethereal acetate derived from the free alcohol; the acetate derived from the alkyl oxide is formed in

smaller quantity. For example, when sodium propoxide and methyl alcohol act on ethyl acetoacetate, the chief product is methyl acetate; propyl alcohol and propyl acetate are also formed. Sodium carbonate, acetate, and resacetate are produced in all these reactions.

Ethyl acetoacetate is not decomposed by ethyl or propyl alcohol at 180°, but on the addition of a small quantity of sodium alkyl oxide the acetoacetate is completely decomposed, yielding ethyl- or propyl-acetate.

Resacetic acid, $C_{18}H_{22}O_5$, is a brown resinous substance, insoluble in water but freely soluble in alkalis. It is reprecipitated on the addition of mineral acids. The sodium and potassium salts are amorphous; they dissolve freely in water, forming neutral solutions.

Geuther obtained two amides ($C_6H_{11}NO_2$ and $C_8H_{15}NO_2$) by treating ethyl acetoacetate with aqueous ammonia (*Jena. Zeitschr.*, **6**, 576). The former is soluble, the latter insoluble in water. The soluble amide melts at 90° and may be heated at 180° without undergoing any further change. At a higher temperature, it splits up into diethyl ketone, ammonium carbonate, and carbonic anhydride. It is also decomposed into diethyl ketone and ammonia by water at 200°. At 240° the diethyl ketone splits up into ethane and carbonic anhydride. Attempts to obtain a pyridine base by the action of hydrogen chloride, calcium chloride, zinc chloride, phosphoric oxide, or phosphoric chloride were unsuccessful. Diethyl ketone was produced in each case.

On fusion with potash, the amide yields equivalent quantities of potassium butyrate and acetate. The constitution of the amide may consequently be represented by the formula OEt·CMe : CH·CONH$_2$.

The products of the action of phosphoric chloride on ethyl-acetoacetate are ethylmonochlorocrotonic acid, and the ethylic salts of mono- and di-chlorethylacetoacetic acids. The acid $C_6H_9ClO_2$ forms colourless needles soluble in alcohol, ether, and in hot water. It melts at 49·5° and boils at 215°. The chlorine is not replaced by nascent hydrogen. The sodium and barium salts do not crystallise. The calcium salt, $Ca(C_6H_8ClO_2)_2 + 2H_2O$, forms colourless prisms. The ethylic salt boils at 184—185°. It is miscible with alcohol and ether, but not with water.

Ethyl chlorethylacetoacetate boils at 192·5° (corr.) and is insoluble in water. Its sp. gr. at 15° is 1·0523. *Ethyl dichlorethylacetoacetate* boils at 220—225°, and has a sp. gr. of 1·183 at 15°.

Rücker (*Annalen*, **201**, 56) states that methylchlorocrotonic acid and the ethylic salt of this acid are the products of the action of phosphoric chloride on ethylic methylacetoacetate. The author, however, finds that methylchlorocrotonic acid is formed, together with the ethylic salts of mono- and di-chloromethylacetoacetic acids. The former, $C_7H_{11}ClO_3$, boils at 179—181°. Its sp. gr. is 1·093 at 15°, the latter, $C_7H_{10}Cl_2O_2$, distils with decomposition between 210° and 220°. Its sp. gr. is 1·225 at 15°. *Ethyl ethoxyethylacetoacetate* and *ethyl ethoxymethylacetoacetate* are formed by the action of an alcoholic solution of sodium ethoxide on ethyl monochlorethyl- and methyl-acetoacetates. The former, OEt·CH$_2$·C(OEt) : CH·COOEt, boils at 210° (corr.), and has a sp. gr. of 0·957 at 22°. The latter,

OEt·CH$_2$·C(OMe) : CH·COOEt,

boils at 190—195°; sp. gr. 0·976 at 22°. These compounds are decomposed by alcoholic sodium hydroxide at 120°, yielding *ethoxyethylacetone*, $OEt{\cdot}CH_2CO{\cdot}CH_2Et$, boiling at 112—115°, and *ethoxymethylacetone*, $OEt{\cdot}CH_2{\cdot}CO{\cdot}CH_2Me$, boiling at 100—105° respectively.

W. C. W.

So-called Ethyl Carbacetoacetate. By N. Polonoffska (*Ber.*, **19**, 2402—2406).—By the action of strong sulphuric acid on ethyl acetoacetate, Hantzsch has obtained besides ethyl isodehydracetate, $C_{10}H_{12}O_4$, a substance of the formula $C_{18}H_{22}O_9$, which may be regarded as a mixed anhydride of the ethereal salt with isodehydracetic acid, thus: $O(CO{\cdot}C_6H_8O{\cdot}COOEt)_2$ (Abstr., 1883, 1083). It is further probable that the so-called ethyl carbacetoacetate, $C_8H_{10}O_3$, obtained by Duisberg from ethyl acetoacetate and hydrochloric acid is identical with ethyl isodehydracetate. In this paper it is shown that the action of hydrochloric is precisely similar to that of sulphuric acid, resulting in the formation of the anhydride, decomposed by alkalis into isodehydracetic acid and its ethyl salt. It follows that the supposed ethyl carbacetoacetate of Duisberg is in reality the ethyl salt of isodehydracetic acid. V. H. V.

Diundecylenic Acid. By P. Brunner (*Ber.*, **19**, 2224—2228, compare Abstr., 1885, 373).—Bromine acts on diundecylenic acid with formation of a *compound*, $C_{22}H_{40}Br_2O_4$; it is an almost colourless oil. When diundecylenic acid is heated with caustic potash at 120° to 130° and the product acidified, a mixture of acids is obtained consisting of undecylenic acid (about one-third of the whole) and other higher acids. These experiments point to the constitution $C_{10}H_{19}{\cdot}CO{\cdot}O{\cdot}C_{10}H_{20}{\cdot}COOH$ for diundecylenic acid. This constitution is further supported by the fact that diundecylenic acid is formed by the action of silver undecylenate on iodundecylenic acid.

Bromundecylenic acid, $C_{11}H_{21}BrO_2$, is obtained by the action of hydrobromic acid on undecylenic acid; it melts at 35°.

Iodundecylenic acid, $C_{11}H_{21}IO_2$, is a colourless, crystalline substance melting at 24°.

When the caoutchouc-like substance obtained by the distillation of castor-oil or of undecylenic acid is heated with alcoholic potash solution at 160°, the product is found to contain undecylenic acid and an acid boiling at 230° to 240°. The greater part of the product does not distil without decomposition. N. H. M.

Ethoxalic Chloride. By R. Anschütz (*Ber.*, **19**, 2158—2160).—Following out his work with Schönfeld (this vol., p. 785), the author finds that the ethoxalic chloride obtained by v. Richter (Abstr., 1879, 138) by the action of phosphoric chloride on ethyl oxalate is really due to a secondary reaction. If the product of the reaction be distilled under reduced pressure (15—16 mm.), *diethyl dichloroglycollate*, $OEt{\cdot}CCl_2{\cdot}COOEt$, distils over at 88—89° as a colourless liquid. When this substance is heated to 165—170° ethyl chloride is evolved, and the remaining liquid is then ethoxalic chloride, the boiling point of which the author found to be 134—135°. The reaction is therefore strictly analogous to that in the propyl series. By this means the

chloride can be easily obtained free from phosphoric chloride, as the glycollate is easily separated therefrom by fractional distillation. By Richter's method this separation was difficult, as the boiling points of ethoxalic and phosphoric chlorides lie so near together. L. T. T.

Hydropyrocinchonic (Symmetrical Dimethylsuccinic) Acid. By C. A. Bischoff and C. Rach (*Annalen*, **234**, 54—89).—Symmetrical dimethylsuccinic acid crystallises in four-sided plates which melt between 186° and 188°. The normal potassium salt yields crystalline precipitates with calcium, barium, silver and lead salts. It also produces precipitates in solutions of copper sulphate and ferric chloride. On dry distillation, the acid yields a characteristic anhydride melting at 87°. The dimethylsuccinic acid which Hardtmuth (Abstr., 1878, 782) obtained from ethyl α-β-dimethylacetosuccinate was impure, hence its low melting point (166°). The syntheses of the acid from ethyl α-β-dimethylethenyltricarboxylate, and also from ethylic dimethylacetylenetetracarboxylate have already been described by the authors (Abstr., 1885, 585).

By the action of an ethereal solution of iodine on ethylic methylsodomalonate, ethylic dimethylacetylenetetracarboxylate and a lower boiling liquid are obtained. Under 760 mm. pressure the latter compound boils at 192°, giving off iodine vapour. It also decomposes on distillation in a vacuum. The authors consider that this substance may possibly be ethyl α-iodopropionate, its formation being represented by the equations $CMe(COOEt)_2Na + I_2 = NaI + CMe(COOEt)_2I$ and $CMe(COOEt)_2I = C_2H_4 + CO_2 + CHMeI{\cdot}COOEt$.

The authors regard cinchonic acid as β-γ-dicarboxy-δ-valerolactone, and agree with Beckurts and Otto (Abstr., 1885, 753) in considering pyrocinchonic anhydride to be the anhydride of dimethylmaleic acid.

W. C. W.

Action of Hydrocyanic Acid on Ethyl Acetosuccinate. By C. Rach (*Annalen*, **234**, 35—43).—The cyanhydrin of ethyl acetosuccinate is obtained by slowly adding the theoretical quantity of strong hydrochloric acid to a mixture of 21·6 grams of the ethylic salt dissolved in ether and 32·5 grams of potassium cyanide dissolved in water. The crude ethereal solution of the cyanhydrin is poured into three times its volume of strong hydrochloric acid. Ammonium chloride is deposited, and the acid mother-liquor is extracted with ether. *β-γ-Dicarboxy-γ-valerolactone*, $C_7H_8O_6$, is obtained by boiling with potash the oily liquid which remains on evaporating the extract. If the aqueous solution of the lactonic acid is treated with calcium or barium carbonates, amorphous salts of the composition $BaC_7H_6O_6$ and $CaC_7H_6O_6$ are obtained. If the latter is boiled with milk of lime a salt of the composition $Ca_3(C_7H_7O_7)_2$ is formed. An analogous barium salt can also be prepared. On distillation at 180°, the valerolactone splits up, yielding *pyrocinchonic anhydride*, identical with the dimethylfumaric anhydride, $C_6H_6O_3$, which Roser obtained (Abstr., 1882, 1114) by the oxidation of oil of turpentine. The anhydride unites with ammonia and with aniline, forming crystalline compounds. The former, $C_6H_7O_2N$, melts at 113°, and the latter, $C_{12}H_{11}O_2N$, at 96°.

On reduction with zinc-dust and sulphuric acid, the anhydride is converted into an acid, $C_6H_{10}O_4$. This substance crystallises in transparent prisms, and melts with decomposition at 186—187°, forming the anhydride $C_6H_{10}O_4$, which melts at 87°. W. C. W.

Asparagine. By A. Piutti (*Compt. rend.*, **103**, 134—137).—The mother-liquor from crude asparagine was concentrated and allowed to stand, when it deposited a mixture of crystals of ordinary asparagine with crystals of a new isomeride. The two varieties are separated mechanically. They are identical in every respect except in the position of the hemihedral faces, the crystals of ordinary asparagine being left-handed, whilst those of the new isomeride are right-handed. Moreover, the new variety has a dextrorotatory power of exactly the same magnitude as the lævorotatory power of ordinary asparagine, and a solution of the two in equivalent proportions is optically inactive. The derivatives (aspartic acid, malic acid, carbamidosuccinic acid, &c.) from both varieties are identical in their chemical properties, but where the compounds are optically active, those derived from ordinary asparagine are lævogyrate, whilst those derived from the isomeride are dextrogyrate to exactly the same extent. It would seem that the two varieties of asparagine are physical isomerides, but the dextrogyrate variety has a much sweeter taste than ordinary asparagine, and although a solution of the two in equal proportions is inactive, the two varieties separate on crystallisation, twinning frequently taking place between the right- and left-handed crystals. The two aspartic acids may, however, be regarded as true physical isomerides, since they combine in equal proportions to form inactive asparagenic acid, which forms monoclinic crystals. C. H. B.

Colour-bases from Furfuraldehyde. By H. Schiff (*Ber.*, **19**, 2153—2155; compare this vol., p. 612).—The best method of preparing furfuralcohol is by decomposing furfuraldehyde with aqueous potash, employing 5 grams potash and 10 c.c. water to each 10 c.c. of the aldehyde.

Furfuralcohol gives no colour-reaction with amidobenzoic acid, β-naphthylamine, or leucaniline sulphate, but with aniline, it yields a yellow compound, $C_{11}H_{11}NO$. This is soluble in alcohol: the solution when treated with aniline hydrochloride yields reddish-green scales of a compound $C_{11}H_{11}NO,C_6H_7N,HCl$.

Furfuraldehyde when treated with phosphoric chloride loses its characteristic odour, and becomes dark-green in colour. The author was, however, unable to separate the excess of phosphoric chloride from the chloride undoubtedly formed. The product of the reaction is soluble in ether, benzene, &c. With both the original product and its solutions, reaction sets in after a time, a solid black condensation product being formed. The solution of the original product forms colouring matters with both aniline and dimethylaniline. When the black solid substance is decomposed with water, a substance $C_{10}H_6O_3 = 2C_5H_4O_2 - H_2O$ is formed which is insoluble in most solvents.

L. T. T.

Action of Phosphoric Sulphide on Complex Furfurane-derivatives. By A. Hantzsch (*Ber.*, **19**, 2400—2402).—With the view of converting furfurane-derivatives into those of thiophen, the action of phosphoric sulphide on ethylic methylcoumarilate (this vol., p. 707) was investigated. There is thus formed ethyl methylthiocoumarilate, $C_8H_4MeO{\cdot}COSEt$, by the direct displacement of the oxygen by sulphur. It crystallises in yellow, soluble needles, melting at 90—91°, sparingly soluble in alcohol, but readily in ether. On treatment with alkali, the reverse displacement of oxygen by sulphur takes place. These changes are analogous to those of coumarin investigated by Tiemann (this vol., p. 880). *Methylcoumarilamide*, $C_8H_4MeO{\cdot}CONH_2$, obtained from the ethyl salt by excess of alcoholic ammonia in presence of a small quantity of zinc chloride, crystallises in small needles which melt at 145°. When boiled with alkalis, it is converted into methyl coumarilic acid. V. H. V.

β-Thiënylglyoxylic Acid and its Derivatives. By W. P. Bradley (*Ber.*, **19**, 2115—2123).—The above acid being an important substance as forming the starting point of very many researches in the thiophen series, the author has investigated it closely. The acid was prepared as described by Peter (Abstr., 1885, 764) by the oxidation of β-acetothiënone. As small quantities of β-thiophenic acid are also almost always produced, the thiënylglyoxylic acid (being the stronger of the two) was purified by fractional neutralisation. Crystallised from water, the acid melts at 58—59°, but when kept over sulphuric acid the melting point rises gradually to 91·5° (Peter gives 86°). This is due to the undried acid containing 1 mol. of water of crystallisation. A number of the salts are described, most of which contain water of crystallisation. The author considers that the water contained in the free acid and in the silver salt is probably water of hydration, $C_4SH_3{\cdot}C(OH)_2{\cdot}COOH$, rather than water of crystallisation. The *methyl salt* melts at 28·5°; the *ethyl salt* is an aromatic oil boiling (with partial decomposition) at 264—265°, and still liquid at −20°. An attempt to obtain the chloride was unsuccessful, β-thiophenic chloride being formed. The *amide* forms white needles easily soluble in alcohol and ether, very sparingly so in water, and melts at 88°. With phenylhydrazine, the acid yields the *phenylhydrazid*, crystallising in intensely yellow needles, soluble in ether and melting at 164—165°.

Peter obtained isonitrosothiënylacetic acid by treating sodium β-thiënylglyoxylate with free hydroxylamine. The author, however, obtained a much better yield by treating the free acid with hydroxylamine hydrochloride. At the same time, a small quantity of oil boiling at 180—190° was obtained, but not further investigated. Several salts of the acid are described. The *methyl* and *ethyl salts* both crystallise in needles, the former melting at 104—105°, the latter at 122—123°. When treated with tin and hydrochloric acid, this acid yields *amidothiënylacetic acid*, $C_4SH_3{\cdot}CH(NH_2){\cdot}COOH$. This crystallises in scales which decompose at 235—240° without previous fusion. The *hydrochloride* crystallises from alcohol in glistening scales. Several salts are described. L. T. T.

Aromatic Hydrocarbons of Caucasian Petroleum. By W. Markownikoff (*Annalen*, **234**, 89—115).—In a previous communication (Abstr., 1884, 1276) the author has pointed out that *naphthenes* form the chief constituents of that portion of Caucasian petroleum which boils below 300°. The petroleum boiling between 85° and 250° contains benzene, toluene, isoxylene, paraxylene, pseudocumene, mesitylene, durene, isodurene, and other isomerides of the formula $C_{10}H_{14}$, diethyltoluene, and isomerides, also hydrocarbons of the composition $C_{11}H_{14}$, $C_{11}H_{12}$, $C_{12}H_{14}$, and $C_{13}H_{14}$. W. C. W.

Bromo-substitution-compounds of the Aromatic Series. By E. Werner (*Bull. Soc. Chim.*, **46**, 275—284).—When chlorine, bromine, iodine, nitric acid or sulphuric acid acts on mono-substitution-derivatives of benzene, the di-derivatives most readily formed and most stable are the para-compounds, next in order stand the ortho and lastly the meta; among tetra-substitution-compounds those of the type 1. 2. 4. 6 are most readily formed, the hydrogens 3. and 5. of the benzene-ring appearing to be particularly difficult to displace. When metacresol and metahydroxybenzoic acid are acted on by bromine-water, tribromometacresol and tribromometahydroxybenzoic acid are formed, the remaining hydrogen-atom not being displaced, even when the bromine is present in large excess, although the hydrogen of the hydroxyl molecule is displaced by bromine; if, however, ortho-substituted-compounds are treated in a similar manner, only two atoms of hydrogen can be substituted; thus, orthohydroxybenzaldehyde only yields $OH{\cdot}C_6H_2Br_2{\cdot}COH$, whilst the presence of a large excess of bromine only results in the substitution of the hydrogen in the hydroxyl group and oxidation of the aldehydic groups, bromoxytribromophenol being formed, and no substitution of the hydrogens occupying the positions 3. 5. being effected; similar reactions occur with parahydroxybenzaldehyde; para- and ortho-cresol in like manner yield dibromocresol, and with a large excess of bromine bromoxytribromophenol is formed, the hydrogens of the positions 3. and 5. remaining unacted on.

The author has made calorimetrical estimations of the heat of substitution of the different hydrogens in the benzene-ring, and finds that in a mono-substituted benzene 1·1 cal. are absorbed, when the hydrogen occupying the para-position is displaced by bromine, whilst if in the compound thus formed hydrogens in the ortho-position be likewise substituted, 3·0 cal. are absorbed, and lastly, that in the substitution of the third hydrogen-atom in one of the meta-positions (3.) by another atom of bromine 5·0 cal. are absorbed. By an application of the above data, the author points out that isomeric compounds of the hexacarbon-ring may be distinguished; thus, a metabromo-derivative when treated with bromine yields a tetrabromo-derivative, whilst the ortho- and para-derivatives merely yield a tribromo-derivative; the two latter may be distinguished by examining their heats of formation.

Further, the heat of transformation of one isomeride into another may be experimentally determined, for if two isomerides yield the same product under the action of the same reagent, the difference of

the total thermal effects produced in the reaction expresses the reciprocal heat of transformation of the two isomerides: thus both ortho- and para-bromaniline are converted into tribromaniline by the action of the theoretical amount of bromine, and the difference between the heats of formation of the tribromaniline from the two isomeric bromanilines is the heat of transformation of the one isomeride into the other; by an application of this to the hydroxybenzoic acids, the author finds that the heat of transformation of the ortho- into the para-compound is + 1·2 cal. A. P.

Derivatives of Hexamethylbenzene and Durene. By A. Colson (*Bull. Soc. Chim.*, **46**, 197—199).—On treating hexamethylbenzene with phosphoric chloride by Colson and Gautier's method (this vol., p. 231), several hexachlorides are formed. The first of these, which probably has the constitution $C_6(CH_2Cl)_6$, forms colourless, flattened, hexagonal crystals, melts at 269° with partial sublimation, and is almost insoluble in ether and chloroform; its sp. gr. = 1·609 at 15°; on boiling with slightly alkaline water, the chlorine is very slowly removed, and a neutral inodorous compound which has no reducing properties and is probably an alcohol, is formed; it melts at 180°, forms salts with acids, and is readily soluble in alcohol, but almost insoluble in water and ether; its aqueous solution is extremely bitter. The second hexachloride, probably having the constitution $CCl_3 \cdot C_6Me_2(CH_2Cl)_3$, is crystalline, melts at 147°, is more readily acted on by alkalis than the former compound, a substance being formed which has a bitter taste and probably alcoholic functions.

By acting on durene with phosphoric chloride in a similar manner, a colourless, pearly, crystalline compound, $C_{10}H_{10}Cl_4$, is formed; it melts at 144°, and its sp. gr. is 1·479. On hydrolysis, it yields a viscous, bitter liquid, sparingly soluble in water or ether, but soluble in acids, with which it forms salts on heating. A. P.

Derivatives of Cymene. By G. Mazzara (*Gazzetta*, **16**, 191—195).—In the course of some experiments made with a view of transforming derivatives of thymol into those of carvacrol, the following derivatives of cymene were prepared. Dinitrobromocymene is formed, together with a mononitro-compound, by the gradual addition of bromocymene (prepared from thymol and phosphoric bromide) to nitric acid, sp. gr. = 1·5; the two are separated by distillation in a current of steam, when the mononitro-compound passes over as a yellow oil. The *dinitro-derivative*, $C_6HMePrBr(NO_2)_2$, crystallises in yellow needles of musk-like odour, melting at 94°. It is isomeric with the dinitrobromocymene of Gerichten, obtained by the nitration of bromocymene prepared by the bromination of cymene; it is readily reduced by zinc and hydrochloric acid, and the resulting amidohydrochloride on oxidation with ferric chloride yields a mixture of bromohydroxy- and dihydroxy-thymoquinone. The *mononitrobromocymene*, $NO_2 \cdot C_6H_2MePrBr$, is a yellow oil of strong musk-like odour, soluble in benzene and ether, sparingly soluble in alcohol; it is isomeric with Gerichten's compound. On reduction, it yields an amidobromocymene as a red oil, volatile in the vapour of water; the sulphate and hydro-

chloride are sparingly soluble in water; their solutions readily assume a violet coloration. *Bromhydroxycymene*, $C_6H_2MePrBr{\cdot}OH$, obtained from the amido-compound by Griess' reaction, is a heavy yellow oil of pleasant odour, decomposed by distillation with evolution of hydrogen bromide. Its constitution is

$$[Me : Br : Pr : OH = 1 : 3 : 4 : 6 \text{ or } 1 : 3 : 4 : 2].$$

Experiments are in progress to decide between the alternative formulæ. V. H. V.

Nitration of Cymene. By A. F. Holleman (*Rec. Trav. Chim.*, **5**, 184—186).—In the course of the nitration of cymene, a substance is formed which is considered by some to be a nitrocymene, by others to be of a different nature. Elementary analysis points to the formula $C_9H_9NO_2$; but owing to its explosive nature its vapour-density cannot be determined. By alkalis and acids, it is decomposed with formation of 1 : 4 toluic acid. On reduction with zinc and acetic acid, it yields a compound C_9H_9O, which crystallises in colourless needles melting at 159°, and is insoluble in most menstrua. This latter substance, heated with a solution of ammonium acetate in acetic acid, forms a nitrogen compound, $C_{18}H_{17}N$, and with phosphoric sulphide a sulphur compound giving the isatin reaction. It would seem that the above reduction product belongs to the class of diacetones, which with dehydrating agents yield derivatives of furfurane, with ammonium acetate those of pyrroline, and with phosphoric sulphide those of thiophen. V. H. V.

Benzene-derivatives. By A. Hand (*Annalen*, **234**, 129—159).—1. *The so-called "fourth" monobromophenol.*—The liquid monobromophenol (b. p. 236—238°) which Fittica (Abstr., 1884, 55) obtained by brominating a cold alcoholic solution of phenol is proved to be impure parabromophenol. If the small quantity of water contained in the liquid is removed by leaving the substance in a desiccator over sulphuric acid for some days, the introduction of a small crystal of parabromophenol will cause the liquid to crystallise. The crystals melt at 64°, and are identical in every respect with parabromophenol. This substance crystallises in quadratic pyramids, $a : c = 1 : 0{\cdot}4644$. The crystals are optically biaxial.

2. *Diazo-compounds.*—Attempts to prepare orthodiazoamidobenzoic acid by the action of nitrous acid on anthranilic acid dissolved in alcohol or nitric or sulphuric acid were unsuccessful. Orthodiazobenzoic nitrate is formed in the case of the acid solutions. The perbromides of ortho- and meta-diazobenzoic nitrates are obtained by the action of bromine dissolved in hydrobromic acid on the corresponding diazo-nitrates. They are decomposed by boiling with alcohol, yielding ortho- and meta-bromobenzoic acids, which melt at 149° and 154° respectively.

3. *Metamerism in benzene-derivatives.*—The bromotoluidine obtained from metabromoparacetotoluidine, yields metabromotoluene when its alcoholic solution is treated with nitrous acid. This result confirms Wroblewsky's statement (Abstr., 1878, 977) that when paracetotoluidine is brominated, the bromine-atom takes the position next to

the amido-group. *Metabromometanitroparacetotoluidine*, formed by nitrating metabromoparacetotoluidine, crystallises in needles of a pale yellow colour. It melts at 210·5°. On treatment with alcoholic potash, *metabromometanitrotoluidine* is obtained. This substance melts at 65°, and is identical with *metanitrometabromoparatoluidine*, obtained by nitrating paracetotoluidine, and brominating the metanitrotoluidine derived from the product. W. C. W.

Derivatives of Chlorinated Paranitrophenols. By A. Kollrepp (*Annalen*, **234**, 1—34).—Crude paranitrophenol may be readily purified by solution in hot, strong, hydrochloric acid. The black tarry matter remains undissolved, and can easily be got rid of by decantation. On cooling, the nitrophenol is deposited. The most convenient mode of chlorination is the following:—25 grams of fused nitrophenol is brought into a strong flask, and dissolved in 1 litre of warm, strong, hydrochloric acid. On cooling, the nitrophenol is deposited in crystals. The flask is fitted with a doubly perforated stopper, a tap funnel passes through one hole, and a bent glass tube through the other. The flask is exhausted by means of an air-pump, and a solution of 7·344 grams of potassium chlorate in 150 c.c. of water is introduced through the tap funnel; towards the end of the operation the flask must be shaken briskly.

On reduction with tin and hydrochloric acid, orthochloroparamidophenol hydrochloride is obtained in rhombic plates. The free base melts at 153°, and dissolves in alcohol, ether, and in hot water. The solutions of the base and of its salts are unstable; to prevent decomposition, sulphuretted hydrogen must be passed through the solution during evaporation. The *sulphate*, $(OH{\cdot}C_6H_3Cl{\cdot}NH_2)_2H_2SO_4 + 2H_2O$, crystallises in white scales, sparingly soluble in cold water. The *oxalate*, $(OH{\cdot}C_6H_3Cl{\cdot}NH_2)_2H_2C_2O_4 + 3\frac{1}{2}H_2O$, forms white needles, soluble in water. The *tartrate*, $(OH{\cdot}C_6H_3Cl{\cdot}NH_2)C_4H_6O_6$, forms sparingly soluble monoclinic crystals.

Dichloroparanitrophenol is best prepared by an analogous process to that used for the mono-derivative: 14·688 grams of potassium chlorate are required for the chlorination of 25 grams of nitrophenol. In addition to the salts which have already been described by Seifart (*Annalen*, Supp. **7**, 198) and Armstrong (this Journal, 1871, 1112), the author has prepared the following:—$NO_2{\cdot}C_6H_2Cl_2{\cdot}OK + H_2O$, which forms orange-coloured needles, sparingly soluble in cold water;

$$(NO_2{\cdot}C_6H_2Cl_2{\cdot}O)_2Cd + 3\tfrac{1}{2}H_2O,$$

golden-yellow crystals; and $(NO_2{\cdot}C_6H_2Cl_2{\cdot}O)_2{\cdot}Cu + 5H_2O$, yellowish-green needles, are obtained by precipitation. They are both soluble in hot water.

Dichloroparamidophenol melts at 167°. The hydrobromide forms hexagonal plates, sparingly soluble in cold water. The oxalate crystallises in white needles, and the nitrate in violet-coloured rhombic plates. Both salts dissolve in hot water.

Attempts to prepare trichloronitrophenol by the method used in the preparation of the mono- and di-derivatives were unsuccessful.

Monochloroquinone can be easily prepared by adding an aqueous

solution of potassium chromate to a feebly acid solution of chloramidophenol sulphate. The solution changes from blue to violet and brownish-red. The reaction is then complete. Dichloroquinone can be prepared from dichloramidophenol by the same method.

A convenient process for preparing *monochloroquinonechlorimide* is to add metallic tin to the crude product of the chlorination of nitrophenol. When the tin is dissolved, the solution is diluted with twice its bulk of water, and cooled to 0°. A solution of bleaching powder is added, when the mixture becomes red, and on the further addition of bleaching powder solution it turns milky, and finally yellow. The chloroquinonechlorimide is deposited in small yellow crystals. Dichloroquinonechlorimide can be prepared by a similar method.

Chloramidophenolsulphonic acid, $OH{\cdot}C_6H_2Cl(NH_2){\cdot}SO_3H$, is prepared by the action under pressure at the ordinary temperature of a concentrated solution of hydrogen sodium sulphite on chloroquinonechlorimide made into a paste with water. On crystallisation from hot water, anhydrous needles are obtained, which, if left in contact with water, slowly change into rhombic crystals containing $2\frac{1}{2}H_2O$. The properties of the acid have been described by Bennewitz (*J. pr. Chem.* [2], **8**, 51). The copper, zinc, and nickel salts are crystalline. The same sulphonic acid is obtained by the action of sodium hydrogen sulphite on dichloroquinonechlorimide.

The *chlorodiazophenolsulphonic acid*, $C_6H_3ClN_2SO_4$, is obtained by the action of nitrous acid on chloramidophenolsulphonic acid suspended in water. On passing gaseous hydrogen chloride into the solution, the diazo-compound is precipitated. It is not identical with the paradiazophenolsulphonic acid described by Bennewitz (*loc. cit.*). The acid forms rhombic prisms containing 3 mols. H_2O. The crystals decompose at 170° without melting. On the addition of silver nitrate to an aqueous solution of the diazo-compound, the silver salt, $C_6H_2ClN_2SO_4Ag + 2H_2O$, is slowly deposited in hexagonal plates of a golden hue. The barium salt, $(C_6H_2ClN_2SO_4)_2Ba + 7\frac{1}{2}H_2O$, forms yellow needles.

The addition of bromine-water to an aqueous solution of parachlorodiazophenolsulphonic acid precipitates paradiazochlorobromophenol, $C_6H_2ClBrN_2O$. This substance dissolves freely in warm alcohol, and is deposited from the solution in golden-yellow needles. It explodes when heated at 150°. The *hydrochloride*, $OH{\cdot}C_6H_2ClBr{\cdot}N_2Cl$, crystallises in white needles. It is easily decomposed by water. The *platinochloride* forms yellow scales.

The constitution of chloroquinonechlorimide and dichloroquinonechlorimide may be represented by [O : Cl : NCl = 1 : 2 : 4], and [O : Cl : NCl : Cl = 1 : 2 : 4 : 6], as they can be prepared from chloroparanitrophenol [1 : 2 : 4], and from dichloronitrophenol, 1 : 2 : 4 : 6.

W. C. W.

Derivatives of Thymol. By G. Mazzara and G. Discalzo (*Gazzetta*, **16**, 195—197).—*Bromonitrosothymol*, $OH{\cdot}C_6HMePrBr{\cdot}NO$, obtained by the bromination of nitrosothymol, crystallises in yellow, glistening needles, which melt at 135° with decomposition. *Bromonitrothymol*, similarly prepared, also crystallises in yellow needles, which melt at 100—101°. *Bromamidothymol*, obtained by reduction of the nitroso-deriva-

tive, crystallises in rose-red scales which melt at 90°; it is probably identical with that obtained by Andresen from amidothymoquinone and hydrobromic acid; its hydrochloride crystallises in prismatic needles, and is converted by nitrous acid into *bromothymoquinone*, which crystallises in yellow scales melting at 48°. This compound is reduced by sulphurous acid to *bromothymoquinol*, which forms a mass of white crystals melting at 52—53°; these crystals, after a time, undergo a transformation, becoming red and melting at 37°; the presence of water facilitates this change. V. H. V.

Combination of Chloral with Resorcinol. By H. Causse (*Compt. rend.*, **103**, 347—350).—When equal molecular proportions of chloral and resorcinol are heated with dilute sulphuric acid at various temperatures, the product is a mixture of acicular crystals with a brown flocculent substance which is a product of the alteration of the crystalline compound by the action of the hydrochloric acid liberated during the reaction. The proportion of chlorine in the product varies with the rapidity with which it separates from the liquid, and this rapidity is greater the deeper the colour of the solution.

The crystals give a violet phthaleïn colour with alkalis, and acquire a green fluorescence when exposed to the air. They melt at 260—280°, and if heated at 300°, resorcinol is volatilised and a bulky carbonaceous residue resulting from the decomposition of the brown substance is left.

The brown substance may be removed from the original product by treatment with benzene, in which it dissolves forming a red solution with a violet fluorescence, which yields crystals of resorcinol when concentrated. When the substance is oxidised by means of potassium permanganate, a brown flocculent precipitate separates, and if this is agitated with ether and mixed with an alkaline bisulphite, the liquid is decolorised and on evaporation resorcinol crystallises out.

The crystals may be regarded as derived from a molecular compound of chloral and resorcinol, which resembles an alcoholate, but loses chlorine and yields compounds possessing the property of becoming fluorescent. The brown substance, on the other hand, when heated at 100°, loses chloral and then hydrogen chloride, until all the chlorine is expelled. The same result is brought about by prolonged washing. The brown compound is in all probability a compound of a polymeride of resorcinol with a polymeride of chloral.

C. H. B.

Melting Point of Phloroglucinol. By A. Baeyer (*Ber.*, **19**, 2186—2187).—The author previously mentioned that phloroglucinol prepared from ethyl malonate melts at 217° (*Ber.*, **14**, 3458), whilst Barth and Schreder (Abstr., 1879, 633) and Tiemann and Will (*Ber.*, **14**, 954) ascribed to it respectively the melting points 206° and 209°. A determination made with pure phloroglucinol from maclurine showed that when quickly heated it melts at 218°, whilst when slowly heated the melting point sinks to 209° or even 200°. N. H. M.

Lactucerine. By O. Hesse (*Annalen*, **234**, 243—253).—Lactucerine, extracted from German *lactucarium*, consists chiefly of a

mixture of the acetates of *α*- and *β-lactucerol*. It is easily decomposed by alcoholic potash, and the addition of water to the solution precipitates the crude lactucerols. The dried precipitate is extracted with boiling alcohol, the solution on cooling deposits *α*-latucerol, and the *β*-compound is obtained by evaporating the mother-liquor. The alcohols are purified by conversion into the acetates, which are recrystallised from alcohol and decomposed by alcoholic potash. *α-Lactucerol*, $C_{18}H_{30}O + H_2O$, crystallises in silky needles, resembling caffeïne in appearance. It is freely soluble in chloroform, ether, light petroleum and in hot alcohol. The solutions are dextrogyrate. A pale reddish-yellow coloration is produced when the chloroform solution is shaken with sulphuric acid of sp. gr. 1·76. The alcohol melts at 179°, and can be distilled in a current of carbonic anhydride. The *acetate* melts at 210°. It dissolves freely in chloroform, ether, and light petroleum. The *propionate* melts at 152°. *β-Lactucerol* is deposited in crystals from ether or chloroform, but not from alcoholic solutions. Its action on polarised light is weaker than that of its isomeride. When $p = 4$ $[\alpha]_D = +38{\cdot}2$ for a solution in chloroform. The acetate crystallises in plates or prisms, and melts at 230°.

W. C. W.

Constitution of Nitranilic Acid. By A. Hantzsch (*Ber.*, **19**, 2398—2399).—In order to determine the successive phases in the conversion of dihydroxyterephthalic into nitranilic acid, namely, whether the quinonehydroxyl- and nitro-groups are introduced in the place of the carboxyl-group eliminated, the author has examined the action of fuming nitric acid on basic sodium dioxyquinonedicarboxylate (this vol., p. 77). It is shown that by the reaction nitranilic acid is formed with evolution of carbonic anhydride. Thus the carboxyl-groups are eliminated and nitro-groups substituted for them, the change being as follows: $C_6O_2(OH)_2(CNH)_2 + 2HNO_3 = C_6O_2(OH)_2(NO_2)_2 + 2CO_2 + 2H_2O$. Nitranilic acid is therefore *paradinitrodihydroxyquinone*.

V. H. V.

Partial Amidation of Poly-nitrated Aromatic Compounds by Stannous Chloride. By R. Anschütz and F. Heusler (*Ber.*, **19**, 2161—2162).—When an alcoholic solution of dinitrobenzene is treated with a solution of the calculated amount of stannous chloride in alcoholic hydrochloric acid, metamidobenzene is formed. When orthoparadinitrotoluene is similarly treated, orthamidoparanitrotoluene (Nölting and Collin, Abstr., 1884, 1006) is formed. The stannous chloride thus attacks that nitro-group in dinitrotoluene which is left unattacked when the reduction is brought about by ammonium sulphide.

L. T. T.

Separation of the Toluidines. By A. Wülfing (*Ber.*, **19**, 2132).—The author disputes the value of Lewy's proposed method for separating the toluidines (this vol., p. 872), and states that the preparations (both on the large and small scale) made by Lewy in his (Wülfing's) works were far from pure, the orthotoluidine, for instance, still containing 4 per cent. of paratoluidine.

L. T. T.

Nitrochlorotoluene and Toluidine. By H. GOLDSCHMIDT and M. HÖNIG (*Ber.*, **19**, 2438—2444).—On nitrating parachlorotoluene with sulphuric and nitric acids at a low temperature, it yields two mononitro-derivatives, of which one crystallises in needles melting at 38°, and is thus identical with that obtained by Beilstein and Kuhlberg from nitrotoluidine. Its constitution, therefore, is [Me : NO_2 : Cl : = 1 : 2 : 4].

Chlorotoluidine, $C_6H_3MeCl{\cdot}NH_2$ [Me : NH_2 : Cl = 1 : 2 : 4], formed by the reduction of the above, is a colourless liquid boiling at 237°, and solidifying in a freezing mixture to form a crystalline mass which melts at 21—22°. Its *hydrochloride* crystallises in colourless needles; the *platinochloride* in small golden-yellow needles. The acetyl-derivative forms sparingly soluble crystals which melt at 130—131°. This base is probably identical with that obtained by Engelbrecht.

Chlorotoluidine, $C_6H_3MeCl{\cdot}N_2$ [Me : NH_2 : Cl = 1 : 3 : 4], obtained by the reduction of the second nitrochlorotoluene formed in the process mentioned above, forms white crystals, melting at 28° and boiling at 228—230°. Its hydrochloride crystallises in small colourless tables, and the *acetyl-derivative* in long silky needles melting at 96—97°. Orthochlorotoluene when nitrated and reduced yields the chlorotoluidine melting at 83°, so that the latter is not derived from parachlorotoluene as previously supposed. V. H. V.

The Nitration of Di- and Mono-methylaniline with Dilute Nitric Acid. By K. H. MERTENS (*Ber.*, **19**, 2123—2127).—The author has repeated his former experiments (this Journal, 1877, **32**, 605) and confirms the melting point, 87°, given there for dinitrodimethylaniline (Lippmann and Fleissner and also Weber give 77°). He finds that the isodinitrodimethylaniline is formed in larger proportion the higher the temperature is allowed to rise during the reaction. If the liquid is kept at 0°, only about 2·5 per cent. of the iso-compound is formed.

Dinitrodimethylaniline (m. p. 87°) forms a hydrochloride which, however, gradually loses all its hydrogen chloride when exposed to the air, and is decomposed by water. When this dinitrodimethylaniline is heated with fuming nitric acid, the only product is trinitrophenylmethylnitramine, $C_6H_2(NO_2)_3{\cdot}NMe{\cdot}NO_2$, described by Romburgh (*Rec. Trav. Chim.*, **2**, 109). When the isodinitrodimethylaniline is similarly heated with fuming nitric acid, only *dinitrophenylmethylnitramine*, $C_6H_3(NO_2)_2{\cdot}NMe{\cdot}NO_2$, is formed. This crystallises in pale yellow lamellæ, which explode when heated above 220°. It is only attacked by very strong potash when methylamine is evolved, but although potassium nitrate and nitrite were recognised, the dinitrophenol probably also formed could not be isolated. The corresponding trinitro-compound is readily attacked by potash, trinitrophenol being formed.

When heated with phenol, aniline, glycerol, &c., the dinitronitramine is reduced to *tetranitrodimethylazobenzene*,

$$C_6H_3(NO_2)_2{\cdot}NMe{\cdot}NMe{\cdot}C_6H_3(NO_2)_2.$$

This forms bright red needles decomposing above 200°. When heated with nitric acid, it is reconverted into the nitramine.

Monomethylaniline yields dinitrophenylmethylnitramine when treated with dilute nitric acid. L. T. T.

Oxidation of Diphenylamine. By E. v. Bandrowski (*Monatsh. Chem.*, **7**, 375—382).—Diphenylamine on oxidation with potassium permanganate yields carbonic anhydride, a resinous, and a yellowish-brown, crystalline substance; the characteristic odour of the carbamines also is emitted, but the compound has not been isolated. The yellowish-brown crystalline substance, $C_{18}H_{14}N_2$, melts at 176—180°, is soluble in ether, chloroform, and benzene, but insoluble in water. With mineral acid, it gives a violet-red coloration; in the case of nitric acid, quinone is also produced. It is readily reduced by zinc-dust, taking up a molecule of hydrogen to form a base, $C_{18}H_{16}N_2$, which forms glistening, colourless crystals, melting at 127—129°, and distilling with decomposition at a higher temperature. It is soluble in benzene, ether, and chloroform, insoluble in dilute acids. With sodium nitrite, it gives a cherry-red, and with fuming nitric acid a bluish-red coloration. In this respect it resembles the diphenylparaphenylenediamine (Abstr., 1884, 592) obtained by Calm, as also in the formation of a dinitroso-derivative, $C_{18}H_{14}(NO)_2N_2$, but it differs in its melting point. If this substance be identical with diphenylparaphenylenediamine, it will probably stand to the base $C_{18}H_{14}N_2$ in the same relation that hydrazo- does to azo-benzene, thus: (i) $C_6H_4(NHPh)_2$; and (ii) $C_6H_4N_2Ph_3$; the latter therefore would be diphenylazophenylene. V. H. V.

Action of Ammonium Formate on Benzaldehyde and Benzophenone. By R. Leuckart and E. Bach (*Ber.*, **19**, 2128—2132).—This is a continuation of Leuckart's previous work (Abstr., 1885, 1215). The crystalline substance melting at 52° is formyldibenzylamine, $(C_7H_7)_2\cdot N\cdot COH$; this distils with partial decomposition above 360°. The sparingly soluble substance has not been further investigated. Besides the compounds mentioned by Leuckart (*loc. cit.*) free dibenzylamine, benzylamine, and formylbenzylamine are produced in the action of ammonium formate on benzaldehyde.

When ammonium formate is heated with benzophenone, *formylbenzhydrylamine*, $CHPh_2\cdot NH\cdot COH$, is formed. This substance crystallises in prisms melting at 132° and boiling above 360°. The free base has been already described by Friedel and Balsohn (b. p. 295°, Abstr., 1881, 279). The authors find the melting point to be 91°, and the boiling point 288—289°. It is a colourless oil, which readily absorbs carbonic anhydride from the air and forms a solid carbonate.

Ammonium formate appears to act in a similar way on many aromatic compounds containing the CO-group, and the authors are further investigating the reaction. L. T. T.

Action of Carbon Bisulphide on Metaphenylenediamine. By P. Gucci (*Gazzetta*, **16**, 185—190).—In continuation of experi-

ments on this subject (Abstr., 1885, 156) it is here shown that the reaction between carbon bisulphide and metaphenylenediamine occurs in three distinct stages; firstly, thiocarbonylphenylenediamine thiocarbonate is formed with evolution of hydrogen sulphide; secondly, the former readily gives up a second molecule of hydrogen sulphide to yield dithiocarboxylphenylenediamine; and thirdly, this combines with phenylenediamine to yield dithiocarboxyltriphenylenediamine, thus:—

(1.) $C_6H_4(NH_2)_2 + 2CS_2 = C_6H_4<^{NH}_{NH}>CS{\cdot}CS_2 + H_2S.$

(2.) $C_6H_4<^{NH}_{NH}>CS{\cdot}CS_2 = C_6H_4(NCS)_2 + H_2S.$

(3.) $C_6H_4(NCS)_2 + 2C_6H_4(NH_2)_2 = C_6H_4[NCS{\cdot}C_6H_4(NH_2)_2]_2.$

V. H. V.

Amido-derivatives of Quinone and Quinol. By R. Nietzki and J. Preusser (*Ber.*, **19**, 2247—2249).—*Diamidoquinol hydrochloride*, $C_6H_2(OH)_2(NH_2)_2,2HCl$, is prepared by reducing dinitroquinol (or its diacetyl-derivative) by means of a warm mixture of stannous chloride, hydrochloric acid, and tin. It crystallises in colourless needles, very soluble in water, sparingly in strong hydrochloric acid. The *tetracetyl-derivative*, $C_6H_2(OAc)_2(NHAc)_2$, is obtained by heating the salt with acetic anhydride and sodium acetate; the reaction is violent. It crystallises in needles, sparingly soluble in water and ether, readily in alcohol and glacial acetic acid. It melts at 216°. When treated with dilute caustic alkali solution, a green solution is formed, which yields yellow needles on exposure to air. The new compound is probably *diacetyldiamidoquinone*, $C_6H_2O_2(NHAc)_2$. When reduced, it is converted into *diacetyldiamidoquinol*,

$$C_6H_2(OH)_2(NHAc)_2.$$

The latter crystallises from dilute alcohol in colourless needles melting at 240°. When boiled with strong hydrochloric acid, a black insoluble crystalline substance is obtained, possibly the quinonediamide, $C_6H_2O_2(NH)_2$. N. H. M.

Bromo- and Nitro-substitution Products of Azo-compounds. By J. V. Janovsky and L. Erb (*Ber.*, **19**, 2155—2158).—The bromazobenzene melting at 187°, and previously described (this vol., p. 795), yields orthamidobenzene on reduction, and is therefore orthobromazobenzene, $C_6H_5{\cdot}N : N{\cdot}C_6H_4Br$ [N : Br = 1 : 2]. The second bromazobenzene (m. p. 85°) described (*loc. cit.*) yields a hydrazobromobenzene, crystallising in brilliant, white needles, melting at 63°, and is therefore parabromazobenzene [N : Br = 1 : 4]. The authors also obtained *metabromazobenzene*, [N : Br = 1 : 3], from the mother-liquors; it crystallises in large orange scales, and melts at 53—55°.

L. T. T.

Phenazine. By C. Ris (*Ber.*, **19**, 2206—2208).—Phenazine (Claus, *Annalen*, **168**, 1) can be obtained by heating 2 grams of orthophenylenediamine with the same amount of pyrocatechol for 30 hours at 200—210°; the product is extracted with water and the residue

purified by sublimation. It has all the properties ascribed to it by Claus (*loc. cit.*). The *picrate*, $C_{12}H_8N_2 \cdot C_6H_3N_3O_7$, crystallises in groups of long, bright, yellow needles, sparingly soluble in cold benzene, more soluble in cold alcohol and chloroform. It melts at 180—190°.

N. H. M.

Sodium Phenylhydrazine. By A. Michaelis (*Ber.*, **19**, 2448—2451).—Sodium dissolves in phenylhydrazine with formation of a solid sodium-derivative together with phenylamine and ammonia, the latter products being formed by the action of the replaced hydrogen on the hydrazine, thus: $2PhN_2H_3 + Na_2 = 2PhN_2NaH_2 + H_2$, and (ii) $PhN_2H_3 + H_2 = PhNH_2 + NH_3$. The sodium compound forms a reddish-yellow, transparent powder, which, under some conditions, spontaneously inflames. It deliquesces in the air, and is decomposed by water completely into sodium hydroxide and phenylhydrazin. In order to decide between the two alternative formulæ, $PhNNa \cdot NH_2$ and $PhNH \cdot NHNa$, it was converted by ethyl bromide into the ethyl-derivative, which was shown from its ready conversion into phenyl-ethyltetrazone to be the unsymmetrical ethyl phenylhydrazine, thus confirming the first of the above formulæ. So also with benzyl chloride, the sodium compound forms a benzyl-derivative, as a thick, colourless liquid, forming a soluble crystalline hydrochloride.

V. H. V.

Phenylhydrazine-derivatives. By G. Pellizzari (*Gazzetta*, **16**, 200—207).—*Amidobenzoylphenylhydrazide*, $NH_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot NHPh$, obtained by heating amidobenzoic acid with phenylhydrazine in equimolecular proportions, crystallises in glistening, white scales which melt at 151°.

Formylphenylhydrazide, $(HCO)NH \cdot NHPh$, prepared from formamide, crystallises in white laminæ, melting at 145°; it is very soluble in alcohol, sparingly in ether and cold water. Similarly carbamide and thiocarbamide form phenylsemicarbazide and phenylsemithiocarbazide identical with the compounds obtained from potassium cyanate or thiocyanate and phenylhydrazine sulphate.

Phthalamide and phenylhydrazine react with evolution of ammonia to form *phthalylphenylhydrazine*, $C_6H_4 < \begin{matrix} CO \\ CO \end{matrix} > N \cdot NHPh$, which crystallises in long, transparent needles melting at 179°. If it is warmed with a dilute solution of potash, and the product acidified, phenylhydrazinephthalic acid is precipitated in white, glistening scales, which melt at 163°. This is soluble in alcohol and acetic acid, sparingly soluble in ether and benzene; when boiled in dilute solutions, it is decomposed into phenylhydrazine and phthalic acid.

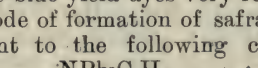
Phthalic anhydride also reacts with phenylhydrazine with elimination of water and formation of a compound isomeric with the above; it melts at 210°, dissolves in alkalis, but is reprecipitated unaltered on addition of an acid; it is not altered even by protracted boiling with concentrated potash solution. It is probable that the former has the constitution of an *amidophthalimide*, $NHPh \cdot N < \begin{matrix} CO \\ CO \end{matrix} > C_6H_4$, and the latter that of a phthalophenylhydrazide, $C_6H_4 < \begin{matrix} CO \cdot NPh \\ CO \cdot NH \end{matrix} >$.

V. H. V.

Hydrazoïnes. By H. Cornelius and B. Homolka (*Ber.*, **19**, 2239—2240).—*Benzhydrazoïne*, $CHPh\langle\begin{smallmatrix}NPh\\|\\NPh\end{smallmatrix}\rangle$, is obtained by heating hydrazobenzene (1 mol.) with benzaldehyde (rather more than 1 mol.) at 120° to 150°, until a drop of the product solidifies when treated with ice-water. It is then steam distilled, the residue dissolved in hot alcohol, and treated with sufficient water to cause a slight turbidity. On cooling, the hydrazoïne separates in lustrous, brownish-yellow plates. It melts at 55°. *Orthonitrobenzhydrazoïne* crystallises in yellowish-red needles melting at 66°. *Metamethylbenzhydrazoïne* forms reddish-yellow needles; it melts at 64°. *Orthohydroxybenzhydrazoïne* forms yellowish-brown plates melting at 58°. *Orthonitrocinnamhydrazoïne* melts at 69°. *Furfurhydrazoïne* crystallises in splendid needles melting at 59°. N. H. M.

Safranine and Methylene-blue. By M. Andresen (*Ber.*, **19**, 2212—2217).—Safranine and methylene-blue are analogous in their behaviour towards alkalis and also towards sulphuric acid, both dissolving in the latter with a green colour. Both fade readily on wool, but last on cotton-wool. Both compounds yield sulphur-derivatives with difficulty. The leuco-compounds both of safranine and of methylene-blue yield dyes very readily when oxidised.

The mode of formation of safranine and the reactions of its derivatives point to the following constitutional formula as the most probable:



N. H. M.

Action of Thiobenzamide on Chloral. By M. Spica (*Gazzetta*, **16**, 182—185).—When a mixture of thiobenzamide and chloral in equimolecular proportions is heated, a crystalline mass of chloral thiobenzamide, $CCl_3\cdot CH(OH)\cdot CPhSNH$, is obtained. It is conveniently purified by solution in alcohol and precipitation by water. It crystallises in yellowish-white needles melting at 104°, of garlic-like odour and intensely bitter taste. It is only sparingly soluble in water, but readily in alcohol, ether and benzene. A similar investigation with butyl chloral did not yield satisfactory results. V. H. V.

Action of Phthalic Anhydride on Amidophenols. By A. Piutti (*Gazzetta*, **16**, 251—255).—In continuation of his experiments on the reaction between amido-compounds and phthalic anhydride, the author has studied the action of the amidophenols on the same substance. When paramidophenol and phthalic anhydride are heated *parahydroxyphenylphthalimide*,

$$OH\cdot C_6H_4\cdot N : C_2O_2 : C_6H_4 \quad [OH : NC_2O_2C_6H_4 = 1 : 4],$$

is produced; it crystallises from acetic acid in glistening laminæ which melt at 287°. It is isomeric with Ladenburg's *hydroxyphthalanilide*. With acetic anhydride, it forms an acetyl-derivative, which

crystallises in needles melting at 238·5°; with potash it yields *hydroxyphenylphthalamic acid*, $OH{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}COOH$, which melts at 289°, and is at the same time reconverted into the original hydroxyphenylphthalimide with loss of 1 mol. H_2O. When treated with concentrated nitric acid, it gives two nitro-derivatives melting at 210° and at 250—260° respectively; the former is a trinitro-compound, $OH{\cdot}C_6H(NO_2)_3{\cdot}N : C_2O_2 : C_6H_4$, and yields with acetic anhydride an acetyl-derivative, crystallising in silky needles melting at 176°.

Similarly triamidophenol (picramine) and phthalic anhydride yield picramine triphthalate,

$$OH{\cdot}C_6H_2(N : C_2O_2 : C_6H_4)_3 \; [OH : (N : C_2O_2 : C_6H_4)_3 = 1 : 2 : 4 : 6],$$

a crystalline substance, melting above 300°, and sparingly soluble in the ordinary menstrua. It dissolves in aqueous potash with evolution of heat and formation of the corresponding *phthalamic acid*, $OH{\cdot}C_6H_2(NH{\cdot}CO{\cdot}C_6H_4{\cdot}COOH)_3$, which crystallises in minute needles melting above 300°. By concentrated nitric acid, it is converted into phthalimide and diphthalyldiamidoquinone, $C_6H_2(N{\cdot}C_2O_2 : C_6H_4)_2O_2$, crystallising in yellow needles which melt at 277°; it is sparingly soluble in alcohol and acetic acid. On reduction with sulphurous acid, it yields the corresponding *quinol*; this crystallises in small glistening prisms, which are soluble in boiling alcohol, infusible at 31°, and yield an acetyl-derivative when treated with acetic anhydride.

V. H. V.

Constitution of Aniluvitonic Acid. By A. Küsel (*Ber.*, **19**, 2249—2250).—When distilled, aniluvitonic yields quinaldine; the acid therefore has the constitution [Me : COOH = : 2 : 4].

Ethyl Quinonedihydroparadicarboxylate. By F. Herrmann (*Ber.*, **19**, 2229—2234).—When ethyl succinosuccinate, dissolved in ice water, is treated with bromine, a compound, $C_{12}H_{16}O_6Br_2$, is obtained. The latter is very unstable, and gives off hydrogen bromide at a low temperature, with formation of ethyl dihydroxyterephthalate. The author considers that this experiment, together with the fact that ethyl succinosuccinate and its derivative containing two atoms of hydrogen less, resemble one another in their physical as well as chemical properties, make it improbable that they are so differently constituted as suggested by Baeyer (this vol., p. 445).

Lehmann has shown (*Ann. Phys. Chem.* [2], **25**, 173) that ethyl quinonedihydroparadicarboxylate exists in three modifications. It separates from the hot solution in aniline in colourless plates; these change their form on cooling, and acquire at the same time a green colour. The most stable form is the rhombic. When the substance is sublimed, a colourless crystalline crust is formed, and this, when rubbed with a glass rod, becomes yellowish-green. The fact of the compound having a colour, although slight, supports the view that ethyl succinosuccinate is a diketone; the colourless modification would then be the true ethyl hydroquinoneparadicarboxylate.

Ethyl succinosuccinate and its derivative with less hydrogen crystallise together, and the crystals and solutions of both substances are fluorescent.

When ethyl quinonedihydroparadicarboxylate is treated with bromine vapour, it becomes white, and is converted into the compound $C_6H_2Br_2O_2(COOEt)_2$. The latter crystallises in large, colourless prisms. When exposed for a long time to the action of bromine, it is converted into ethyl dibromoquinoneparadicarboxylate, which forms sparingly soluble, yellow, lustrous needles. When this is treated with bromine-vapour, it yields tetrabromoquinone.

N. H. M.

Benzene-derivatives from Ethyl Succinosuccinate. By K. Loewy (*Ber.*, **19**, 2385—2398).—In this paper unsuccessful attempts to prepare dihydroxyquinonedicarboxylic acid (dihydroxyquinoneterephthalic acid) from its ethyl salt (this vol., p. 354) are described. A basic sodium salt, $C_6O_2(ONa)_2(COONa)_2 + OH\cdot C_6O_2(ONa)(COONa)_2 + 2H_2O$, was obtained as a sparingly soluble amorphous powder. This, when boiled with hydrochloric or sulphuric acid, yields, in addition to carbonic anhydride, *dihydroxyquinone*, $C_6H_2O_2(OH)_2$ [O : OH : O : OH = 1 : 3 : 4 : 6], which forms blackish-brown crystals, sparingly soluble in water and ether, soluble in alcohol, yielding a deep-red solution.

With nitric acid, ethyl dihydroxyquinonedicarboxylate forms nitranilic acid; with nitrous acid, it yields a compound of the formula $C_{24}H_{25}O_{16}N$ or $C_{24}H_{23}O_{16}N$, probably an oxime; with chlorine, it yields a substance of the formula $C_5H_6Cl_2O_3$, whose constitution is still doubtful; with sulphurous acid, it is reduced to the corresponding *tetrahydroxyterephthalic acid*, $C_6(OH)_4(COOEt)_2$. This latter crystallises in glistening gold leaflets, melting at 178°, sparingly soluble in water, alcohol, and ether; dissolved in a dilute solution of soda, it forms a neutral sodium salt, $C_6(OH)_4(COONa)_2$, which crystallises in prisms, partially decomposed after some time with water. But if the ethyl salt is treated with concentrated soda, a basic sodium salt, $ONa\cdot C_6(OH)_2(COONa)_2$, $C_6(OH)_2(ONa)_2(COONa)_2 + 3H_2O$, is formed. If the mother-liquor from the former of these salts is poured into concentrated sulphuric acid, *tetrahydroxybenzene*, $C_6H_2(OH)_4$ [$(OH)_4 = 1 : 2 : 4 : 5$], is produced. This compound crystallises in small, golden needles, moderately soluble in alcohol and ether; it is rapidly decomposed in acid solutions, with separation of humus-like substances. Its alkaline, alkaline earth, zinc, and silver salts are orange-coloured; the mercurous salt is a red gelatinous precipitate.

V. H. V.

Reduction and Condensation of Homologues of Benzoylbenzoic Acid. By L. Gresly (*Annalen*, **234**, 234—241).—Paratoluenephthaloic acid is converted into paratolylphthalid by reduction with zinc and hydrochloric acid, and into paramethylorthobenzylbenzoic acid by reduction with zinc-dust and ammonia. *Paratolylphthalide*, $CO<^{C_6H_4}_{-O-}>CH\cdot C_6H_4Me$, crystallises in needles, and melts at 129°. It is sparingly soluble in alcohol and insoluble in ammonia. *Metamethylorthobenzylbenzoic acid*, $C_6H_4Me\cdot CH_2\cdot C_6H_4\cdot COOH$, is freely soluble in alcohol, acetic acid, and benzene. It melts at 133·5—134°. The ammonium and barium salts are crystalline and dissolve freely in water

Metaxylenephthalide, $CO<^{C_6H_4}_{-O-}>CH\cdot C_6H_3Me_2$, melts at 83·5—84°. It is sparingly soluble in alcohol, benzene, and acetic acid at the ordinary temperature.

Metadimethylorthobenzylbenzoic acid, $C_6H_3Me_2\cdot CH_2\cdot C_6H_4\cdot COOH$, melts at 157—158°, and is soluble in alcohol. The ammonium salt crystallises in silky scales. The barium salt is sparingly soluble in water. It is deposited from its solution in weak alcohol in crystals containing 1 mol. H_2O.

Mesitylphthalide, $CO<^{C_6H_4}_{-O-}>C_6H_2Me_3$, from mesitylenephthaloylic acid, forms thick needles and melts at 163—164°. *Trimethylorthobenzylbenzoic acid* [1 : 3 : 5] melts at 221°, *pseudocumylphthalide* at 140°, and *trimethylorthobenzylbenzoic acid* [1 : 2 : 4] at 185°.

The phthaloylic acids are converted into anthracene and its homologues by heating with zinc-dust, and into anthraquinone-derivatives by the action of fuming sulphuric acid. Phenylphthaloylic, toluenephthaloylic, metaxylenephthaloylic, and pseudocymenephthaloylic acids respectively yield anthracene, and β-methyl-, dimethyl-, and trimethyl-anthracene.

β-Methylanthraquinone melts at 175°, and is obtained from toluenephthaloylic acid. Meta- and para-xylenephthaloylic acids yield dimethylanthraquinones melting at 180° and 118° respectively.

From pseudocumenephthaloylic acid, *trimethylanthraquinone* and *dimethylanthraquinonecarboxylic acid* are obtained. The former melts at 161°, the latter at 239—240°. W. C. W.

Anisoïlphthaloylic Acid. By C. Nourrisson (*Bull. Soc. Chim.*, **46**, 203—208).—*Anisoïlphthaloylic acid*, $COOH\cdot C_6H_4\cdot CO\cdot C_6H_4OMe$, is prepared by gradually adding 70 grams of aluminium chloride to a mixture of 50 grams of phthalic anhydride with 150 grams of anisoïl, and heating at 100° for 45 minutes. The product is poured into cold water, washed, dissolved in ammonium carbonate, precipitated with hydrochloric acid, and recrystallised several times from toluene. It melts at 141—143°; it cannot be distilled without decomposition, and is readily soluble in the usual solvents, with the exception of water. The sodium, ammonium, hydrogen, potassium, calcium, barium, silver, and copper salts were prepared. On fusing the sodium salt with potassium hydroxide, it is decomposed into benzoic and parahydroxybenzoic acids, the latter being formed by the action of the fused alkali on the anisic acid previously produced. Treated with bromine at 100°, anisoïlphthaloylic acid yields the monobromo-derivative, $C_{15}H_{11}O_4Br$; this melts at 194—196°, is insoluble in water, but dissolves readily in aqueous alkalis, chloroform, or alcohol, and crystallises from acetic acid in short, colourless needles. On acting on anisoïlphthaloylic acid with zinc and hydrochloric acid, a lactone-like compound, $CO<^{C_6H_4}_{-O-}>CH\cdot C_6H_4\cdot OMe$, is formed. It melts at 116—117°, is insoluble in water, but dissolves readily in alcohol, chloroform, and acetic acid, and forms colourless crystals. By reducing anisoïlphthaloylic acid with ammonia and powdered zinc, an acid having the

composition $OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}C_6H_4{\cdot}COOH$, is formed. It melts at 110° to 111°, is insoluble in water, but dissolves very readily in hot alcohol and chloroform; it crystallises in long needles. The *sodium salt* has the composition $C_{15}H_{13}O_3Na + \frac{1}{2}H_2O$. By heating anisoïlphthaloylic acid with sulphuric acid at 160° for six hours, oxyanthraquinone is formed, and on distilling the acid with zinc, it yields anthracene.

On heating anisoïlphthaloylic acid with hydrochloric acid, methyl chloride, phenol toluene, phthalic and acetic acids and a white amorphous compound are formed; the last is probably a phthaleïn, and by fusion with potash yields benzoic and parahydroxybenzoic acids. By heating anisoïlphthaloylic acid with phenol and stannic chloride at 115° to 120°, the phenyl salt is not obtained, but a yellowish-white compound is formed, which softens at 80°, but has no well-defined melting point; it dissolves with a reddish-violet colour in aqueous baryta, soda, or ammonia, and forms a cherry-red solution with sulphuric acid; it is soluble in all the usual solvents.

A. P.

Orthoparadinitrobenzenesulphonic Acid and its Derivatives. By C. Willgerodt and P. Mohr (*J. pr. Chem.* [2], **34**, 113—124).—*Orthoparadinitrobenzenesulphonic acid*, $C_6H_3(NO_2)_2{\cdot}SO_3H$, is prepared by boiling α-dinitrophenyl disulphide with an excess of fuming nitric acid; the product is poured into much water, filtered, and the filtrate evaporated until free from nitric acid. The solution is then kept for some time in a vacuum over sulphuric acid, when long, bright yellow, transparent prisms separate containing 3 mols. H_2O. It melts at 106—108°, dissolves readily in water and alcohol, sparingly in ether, and is insoluble in benzene. When the aqueous solution is treated with excess of alkali, it acquires an intense dark-yellow colour, owing to the formation of a salt of α-dinitrophenol. When the acid is boiled with aniline, dinitrophenylaniline melting at 156° is formed. Alcoholic solution of ammonia acts on the acid under pressure yielding dinitraniline [$NH_2 : (NO_2)_2 = 1 : 2 : 4$], melting at 178°. The acid can be readily converted into dinitrophenyl mercaptan and dinitrodiphenyl bisulphide, by treating an aqueous solution with potassium hydrosulphide in the cold; the product is treated with hydrochloric acid, which precipitates the dinitrophenyl mercaptan. The latter, when boiled in presence of air, is oxidised to the disulphide. The *potassium salt* forms very large, transparent, bright yellow plates, readily soluble in water; it can be heated in water at 150° without decomposition. When strongly heated it detonates. The *ammonium salt* crystallises in groups of yellow lustrous plates; the *barium* (with 2 mols. H_2O), *zinc* (with 6 mols. H_2O), and *lead* (with 3 mols. H_2O) salts, crystallise in bright yellow plates. The *sodium*, *strontium*, and *calcium* (with 2 mols. H_2O) salts were also prepared.

Orthoparadinitrobenzenesulphochloride, $C_6H_3(NO_2)_2{\cdot}SO_2Cl$, is obtained by heating potassium dinitrobenzenesulphonate with phosphorus pentachloride at 160°. It forms clear, prismatic crystals, melting at 102°. The *amide*, $C_6H_3(NO_2)_2{\cdot}SO_2NH_2$, crystallises from ether in long, colourless, lustrous needles which melt at 154°. Caustic potash decomposes it with evolution of ammonia and formation of potassium dinitrophenoxide.

N. H. M.

Sulphobenzidemetasulphonic Acid. By R. Otto (*Ber.*, **19**, 2417—2424).—It has been observed that sulphuric hydroxychloride forms with sulphobenzide a sulphonic acid, thus: $Ph_2SO_2 + OH{\cdot}SO_2Cl = HCl + PhSO_2{\cdot}PhSO_2{\cdot}OH$ (Abstr., 1879, 243). The acid, purified by means of its lead salt, crystallises with $2\frac{1}{2}$ mols. H_2O in feathery masses, readily soluble in water and alcohol. The sodium salt with 3 mols. H_2O, and the ammonium salt crystallise in deliquescent needles, the *potassium* with 3 mols. H_2O, and *calcium* with 7 mols. H_2O in leaflets, the *barium* with 4 mols. H_2O, the *lead* with $3\frac{1}{2}$ mols. H_2O, and the *copper* salt with $7\frac{1}{2}$ mols. H_2O. The *acid* chloride crystallises in needles or rhombs melting at 98—99°, soluble in alcohol and benzene; the *amide* in glistening needles melting at 154°; the *anilide* in warty aggregates melting at 130—131°; the *ethyl* salt in glistening leaflets melting at 89°, soluble in alcohol, insoluble in water; and the *phenyl* salt in small, indistinct crystals melting at 106°. By an indirect method it was shown that the above acid belongs to the meta-series, in that when treated with benzene in presence of a dehydrating agent it yields a phenylene diphenylsulphone identical with the compound obtained under the same conditions from metaphenylenedisulphonic acid. This disulphone, $C_6H_4(SO_2Ph)_2$ [$SO_2Ph : SO_2Ph = 1 : 3$], crystallises in minute needles melting at 190—191°, and distilling at a higher temperature; it is insoluble in water, and somewhat soluble in alcohol and benzene at their boiling points.

Sulphobenzidesulphonic acid when treated with dry chlorine yields sulphuryl chloride and chloro-derivatives of benzene; a similar change occurs with phosphoric chloride; on fusion with alkalis it forms phenol sulphurous acid, together with traces of phenyl mercaptan and a sulphur compound of high boiling point not further examined.

V. H. V.

Decomposition of Sulphobenzide and Sulphotoluide. By R. Otto (*Ber.*, **19**, 2425—2426).—Sulphobenzide and toluide when fused with alkalis are decomposed into sulphurous acid, phenol or paracresol, and diphenyl; from the former small quantities of phenyl sulphide and mercaptan are also obtained as subsidiary products.

V. H. V.

Paraphenolsulphonic Acid. By S. A. Le Canu (*Compt. rend.*, **103**, 385—388).—This acid, prepared by the ordinary method, crystallises in colourless, hydrated, highly deliquescent needles. The potassium salt is obtained by the action of the acid on potassium hydrogen carbonate. It forms anhydrous, hexagonal lamellæ belonging to the rhombic system and melting at 400°.

When a current of air charged with the vapour of the requisite quantity of bromine is passed into a concentrated and well-cooled solution of the acid, and the solution is evaporated in a vacuum, it yields colourless, hydrated, highly deliquescent needles of the composition $C_6H_5BrSO_4 + 2H_2O$. The monosodium salt of this acid crystallises in needles which are anhydrous if dried at 100°.

The dibromo-derivative is obtained in a similar manner, using double the quantity of bromine. It forms crystalline scales which, when dried in dry air, have the composition $C_6H_4Br_2SO_4 + H_2O$. The

continued action of bromine on a solution of the acid or its potassium salt does not yield a tribromo-derivative, sulphuric acid, hydrogen bromide, and tribromophenol being formed in accordance with the equation $C_6H_6SO_4 + 3Br_2 + H_2O = 3HBr + C_6H_3Br_3O + H_2SO_4$.

Heats of Neutralisation.

	1st equivalent, Na_2O.	2nd equivalent, Na_2O.
Paraphenolsulphonic acid.....	+ 13·439	+ 8·960
Monobromoparaphenolsulphonic acid	+ 13·52	+ 10·703
Dibromoparaphenolsulphonic acid ..	+ 13·067	+ 12·634

Paraphenolsulphonic acid has both an acid and a phenolic function. The introduction of bromine has no effect on the thermal value of the first or acidic function, but considerably increases that of the second function. C. H. B.

Action of Bromine on Aqueous Solutions of the Xylenesulphonic Acids. By W. Kelbe and H. Stein (*Ber.*, **19**, 2137—2139).—When an aqueous solution of orthoxylenesulphonic acid, $C_6H_3Me_2{\cdot}SO_3H$ [Me : Me : SO_3H = 1 : 2 : 4], is treated at about 40° with a hydrochloric acid solution of bromine, dibromortho-xylene [Me : Me : Br : Br = 1 : 2 : 4 : 5], bromortho-xylene [Me : Me : Br = 1 : 2 : 4], and bromortho-xylensulphonic acid (Jacobsen, Abstr., 1885, 143), are formed.

Metaxylenesulphonic acid under like conditions yields dibromometaxylene [Me : Me : Br : Br = 1 : 3 : 4 : 6], bromometaxylene, and an acid melting at 130°.

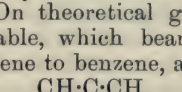
Paraxylenesulphonic acid, now under investigation, appears to give similar results. L. T. T.

Bromoparacymenesulphonic Acids. By A. Claus and A. Christ (*Ber.*, **19**, 2162—2166).—When metabromoparacymene is sulphonated, two sulpho-acids are formed. The chief product is Kelbe and Koschnitzky's α-bromocymenesulphonic acid (this vol., p. 884). The amide prepared from this acid melts at 195° (uncorr.).

Parabromocymene can be prepared by treating an aqueous solution of paracymenesulphonic acid with bromine; the yellow oil obtained is steam distilled and the product boiling between 220° and 250° distilled over potash.

Another *bromocymenesulphonic acid* was obtained by directly brominating paracymenesulphonic acid [SO_3H = 3]. It crystallises in colourless lustrous plates, melting at 180° (uncorr.), and has probably the constitution [Br : SO_3H = 5 : 3]. N. H. M.

Thiopten. By A. Biedermann and P. Jacobsen (*Ber.*, **19**, 2444—2447).—On theoretical grounds the existence of a compound $C_6H_4S_2$, is probable, which bears to thiophen the same relation as that of naphthalene to benzene, and whose constitution is expressible by a formula,



Such a compound (*thiopten*) is obtained in small quantities by the distillation of citric or tricarballylic acid with phosphorus sulphide, and can be purified by means of its crystalline compound with picric acid. It is an oil boiling at 224—226°, of faint, pleasant odour; it gives the indophenine reaction. The *picrate*, $C_6H_4S_2,C_6H_3O(NO_2)_3$, crystallises in golden needles, melting at 133°, and the tetrabromo-derivative, $C_6Br_4S_2$, in long white needles, melting at 172°, soluble in benzene, sparingly soluble in alcohol. V. H. V.

Action of some Organic Chlorides on Diphenyl in Presence of Aluminium Chloride. By P. Adam (*Compt. rend.*, **103**, 207—208).—Diphenyl when subjected to Friedel and Crafts' reaction yields derivatives of the same order as those obtained from benzene.

15 parts of melted diphenyl were mixed with 1 part of aluminium chloride and 1 part of methylene chloride gradually added. A somewhat energetic reaction takes place, and when all the methylene chloride has been added, the mixture is heated on the water-bath to expel all hydrogen chloride, and then poured into water and distilled. In this way diphenylenemethane (fluorene) is obtained, which melts at 113°, boils at 300—305°, and yields a dibromo-derivative melting at 166°, and a tribromo-derivative melting at 161°. The product also contains a certain quantity of a substance which melts at 161°, the melting point of diphenylenediphenylmethane, $(C_6H_4{\cdot}C_6H_5)_2CH_2$.

The action of methyl chloride on diphenyl in presence of aluminium chloride yields a large number of products, which are being investigated. C. H. B.

Occurrence of Acridine. By J. Walter (*J. pr. Chem.* [2], **34**, 134—135).—The last product obtained by distilling crude diphenylamine was found to contain acridine, the presence of which is probably due to orthotolylphenylamine formed from the toluidine which is always present in small quantities in commercial aniline. N. H. M.

Synthesis of Acridine. By R. Möhlau (*Ber.*, **19**, 2451—2453).—The constitutional formula of acridine has been confirmed by its synthesis from diphenylamine and formic acid or chloroform, as also from the condensation of ortholotylaniline. In this paper, a synthesis from aniline and salicylic aldehyde in presence of zinc chloride is described, the reaction being as follows: $PhNH_2 + OH{\cdot}C_6H_4{\cdot}COH = C_{13}H_9N + 2H_2O$. The product was identical in chemical and physical properties with the acridine originally obtained from crude anthracene by Graebe and Caro. It is also shown that parahydroxybenzaldehyde, as also benzaldehyde form acridine with diphenylamine, probably from an intermediate decomposition of the aldehyde into phenol or benzene on the one hand, and formic acid on the other, and this latter substance reacts in accordance with the above-mentioned synthesis. V. H. V.

Action of Nitric Acid on Unsymmetrical Diphenylethane. By R. Anschütz and E. Romig (*Annalen*, **233**, 327—351).—The products of the nitration of unsymmetrical diphenylethane (Abstr.,

1885, 800) are benzophenone, diphenylethyleneglycol mononitrite (m. p. 106°), diphenylvinyl nitrite (m. p. 87°), and a fourth substance which melts at 148—149°. The best yield of *diphenylethyleneglycol mononitrite*, $OH{\cdot}CPh_2{\cdot}CH_2{\cdot}O{\cdot}NO$, is obtained by adding 1 part by weight of nitric acid (sp. gr. 1·5) to a well-cooled solution of diphenylethane (1 part) in 10 parts of glacial acetic acid. After an interval of one hour, the mixture is warmed on a water-bath for 30 minutes, and is then poured into water. The nitrite forms colourless needles or prisms. On oxidation with a mixture of chromic and acetic acids, benzophenone and diphenylvinyl nitrite are produced. The latter compound is also formed by the action of acetic chloride on diphenylethyleneglycol mononitrite, $MeCOCl + Ph_2C_2H_3NO_3 = Ph_2C : CH(NO_2) + C_2H_4O_2 + HCl$.

An aqueous solution of potassium hydroxide has no action on the glycol nitrite at the ordinary temperature, but on boiling complete decomposition ensues. Alcoholic potash splits up the compound into benzophenone and potassium nitrite. When the acetic acid solution is treated with nitric acid, either diphenylvinyl nitrite or the compound melting at 148—149° is formed, according to the temperature at which the reaction takes place.

Diphenylvinyl nitrite, $Ph_2C : CHO{\cdot}NO$, crystallises in rhombohedra [$a : c = 1 : 1{\cdot}0669$]. It is freely soluble in alcohol, ether, benzene, chloroform, and glacial acetic acid. It yields benzophenone on oxidation, and benzophenone and potassium nitrite on treatment with alcoholic potash. The compound melting at 148—149° is formed when a mixture of the acetic acid solution of the nitrite and nitric acid is gently warmed.

A solution of equal quantities of benzophenone and diphenylvinyl nitrite in light petroleum deposits monoclinic tabular crystals, [$a : b = 2{\cdot}4793 : 1$]. The constitution of the substance melting at 148—149° has not yet been ascertained. It can be prepared by the action of nitric acid on an acetic acid solution of diphenylethane or diphenylethylene. It crystallises in monoclinic plates, [$a : b : c = 0{\cdot}59862 : 1 : 0{\cdot}81340$], and dissolves freely in ether, but less readily in benzene and acetic acid. The compound is slowly oxidised by chromic acid, yielding benzophenone. It is also converted into benzophenone when boiled with alcoholic ammonia or potash. When reduced with stannous chloride in alcoholic solution, ammonium chloride, *diphenylacetonitrile*, $CHPh_2CN$, and isodiphenylacetonitrile are formed. The nitrile is deposited from ether in colourless prisms. It melts at 71—72°, and is converted by the action of potassium hydroxide in alcoholic solution into diphenylacetamide and diphenylacetic acid. The amide melts at 165—166°. *Isodiphenylacetonitrile* is soluble in benzene, but insoluble in alcohol. It melts at 167—169°. W. C. W.

Action of Powdered Zinc on Benzyl Chloride. By E. Prost (*Bull. Soc. Chim.*, **46**, 247—250).—If the tarry resinous hydrocarbons formed when benzyl chloride is heated with powdered zinc, are fractionally distilled, they yield phenyltoluylmethane, toluene, a small proportion of unaltered benzyl chloride, anthracene, and a hydrocarbon having the composition C = 92·66 per cent., H = 7·19 per cent., and

which may possibly be the hydrocarbon $C_{21}H_{20}$ described by Zincke (*Ber.*, **7**, 1154). A. P.

Triphenylmethanecarboxylic Acid from Phenylphthalide. By L. Gresly (*Annalen*, **234**, 241—242).—Phenylphthalide readily combines with benzene in the presence of aluminium chloride, forming triphenylmethanecarboxylic acid. Paratolylphthalide unites with benzene in presence of aluminium chloride, forming *paratolyldiphenylmethanecarboxylic acid*, $C_6H_4Me{\cdot}CHPh{\cdot}C_6H_4{\cdot}COOH$. The acid crystallises in needles melting at 154—155°. The barium salt is more soluble in alcohol than in water. The alcoholic solution deposits crystals of the composition $(C_{21}H_{17}O_2)Ba + 2\frac{1}{2}H_2O$. W. C. W.

Aromatic Carbodiimides. By A. Huhn (*Ber.*, **19**, 2404—2414). It has been observed by Weith that the conversion of thiocarbanilide by metallic oxides into diphenylthiocarbamide is conditioned by the presence of water; with dry reagents diphenylcarbamide, $C(NPh)_2$, is produced, which on adding water readily changes into the carbamide. In this paper the corresponding naphthyl and tolyl compounds are described.

α-Carbodinaphthylimide, $C(NC_{10}H_{7\alpha})_2$, is prepared from α-dinaphthylthiocarbamide and mercuric oxide in the dry state and under benzene; it crystallises in combinations of prisms with pyramids, melts at 93—94°, and is readily soluble in benzene, sparingly soluble in petroleum and ether. By aqueous alcohol, it is converted into the corresponding carbamide, by hydrogen sulphide into the thiocarbamide, and by carbon bisulphide into the isothiocarbimide.

β-Carbodinaphthylimide, $C(NC_{10}H_{7\beta})_2$, obtained under similar conditions, forms white crystals melting at 145—146°. As regards its solubility and reactions it resembles the above compound. When boiled with alcohol, it is converted into β-dinaphthylcarbamide. This was also prepared by the action of mercuric oxide on β-dinaphthylthiocarbamide; it crystallises in fine interlaced needles, and melts at 293°.

Carbophenyltolylimide, $NPh : C : NC_7H_7$, from phenylparatolylthiocarbamide, is a light mobile liquid boiling at 325—330°, gradually converted into a vitreous mass, probably from polymerisation; in its reactions with water and hydrogen sulphide, it resembles the above compounds; with carbon bisulphide it yields a mixture of phenyl- and tolyl-thiocarbimides, thus: $NPh : C : NC_7H_7 + CS_2 = CSNPh + CSNC_7H_7$; with aniline it produces the unsymmetrical diphenyltolylguanidine, $NHPh{\cdot}C(NH{\cdot}C_7H_7) : NPh$, which forms a white, horny mass, melting at 126°, soluble in alcohol, ether, and benzene. Its hydrochloride crystallises in needles, and the platinochloride is a red amorphous precipitate.

Carbophenylorthotolylimide, from phenylorthotolylthiocarbamide, is a thick syrup boiling at 320—325°, and gradually solidifying into a vitreous mass which melts at 71°, and finally into a porcelain-like substance. With orthotoluidine, it forms the unsymmetrical guanidine $C_7H_7{\cdot}NH{\cdot}C(NHPh) : NC_7H_7$, crystallising in needles which melt at

123°, readily soluble in alcohol, ether, and benzene; its *hydrochloride* crystallises in colourless prisms, and the *platinochloride* in orange-yellow tables.

The symmetrical *diphenylparatolylguanidine*, $C_7H_7N : C(NHPh)_2$, prepared from paratoluidine and thiocarbanilide in presence of lead oxide, crystallises in interlaced needles melting at 120—121°, and is readily soluble in alcohol, ether, and benzene. The symmetrical *phenyldiorthotolylguanidine* melts at 102°, and resembles the above compound in appearance and solubility. V. H. V.

Thio-β-dinaphthylamine and its Derivatives. By C. Ris (*Ber.*, **19**, 2240—2246).—*Thio-β-dinaphthylamine*, $C_{10}H_6<^{NH}_{S}>C_{10}H_6$, is prepared by gradually heating β-dinaphthylamine (10 parts) and sulphur (2·4 parts) up to 250°; after the mixture has been kept for 10 hours at this temperature, it is dissolved in benzene and boiled with powdered copper. It crystallises in groups of needles which become brown at 232°, and melt at 236°; at a higher temperature, it gives off nitrogen, and carbonises. It dissolves in benzene and cumene, readily in ether and glacial acetic acid. The solution in sulphuric acid is violet; the colour changes to deep blue on adding a drop of nitric acid. The *picrate* forms nearly black, lustrous crystals almost insoluble in alcohol, ether, benzene, &c. It melts with decomposition at 256°.

β-Dinaphthylcarbazole, $NH<^{C_{10}H_6}_{C_{10}H_6}>$, is obtained by heating an intimate mixture of the thio-compound (1 part) with powdered copper (2 parts) in a retort in a current of carbonic anhydride. A reddish-yellow oil distils over, which solidifies to a glassy, brittle mass. It crystallises from benzene in almost colourless needles melting at 170°; it dissolves sparingly in alcohol, readily in ether, and very readily in benzene. Its solution shows an intense bluish-violet fluorescence. The *picrate* crystallises in needles nearly black, and almost insoluble in alcohol, ether, and benzene. It melts at 221°, and is readily decomposed by water. The *acetyl-derivative*, $C_{20}H_{12} : NAc$, crystallises from warm benzene, in which it dissolves readily, in groups of long, yellowish needles which melt at 143°. It is sparingly soluble in ether and alcohol.

Oxy-β-dinaphthylamine, $C_{10}H_6<^{NH}_{O}>C_{10}H_6$, is formed when thio-dinaphthylamine is heated with superficially oxidised copper for two to three hours at 250° to 280°. The product is boiled for a long time with much benzene, and filtered. It is a lemon-coloured, crystalline powder melting at 301°; it dissolves sparingly in alcohol, ether, and glacial acetic acid, readily in cumene. It also dissolves in sulphuric acid, yielding a deep brown solution. The *acetyl-derivative* is prepared by the action of acetic chloride on the substance dissolved in cumene. It is a yellowish substance melting at 235°; it is readily soluble in benzene, almost insoluble in light petroleum and ether.

N. H. M.

Nitronaphthalenesulphonic Acid. By P. T. Cléve (*Ber.*, **19**, 2179—2182).—*γ-Nitronaphthalenesulphonic acid*, $NO_2 \cdot C_{10}H_6 \cdot SO_3H$, is obtained together with the *β*- and *ϑ*-acids by nitrating sodium *β*-naphthalenesulphonate. The product is treated with baryta and extracted several times with boiling water. The intermediate fractions contain the new barium salt. This is converted first into potassium salt, and then into the chloride, which is crystallised from benzene and from glacial acetic acid. A mixture of large and slender needles is obtained; the former have the melting point of the chloride of the *β*-acid. The small crystals are converted into the acid by boiling with water. It forms a yellow mass readily soluble. The *potassium salt* crystallises in sparingly soluble, slender, flexible needles; the *sodium salt* forms pale-yellow needles; it is rather soluble; the *barium* and *lead salts* (both with 3 mols. H_2O) and a *double salt* with lead acetate were prepared. The *ethyl salt* crystallises from alcohol in pale-yellow slender needles melting at 114·5°. The *chloride*, $NO_2 \cdot C_{10}H_6 \cdot SO_2Cl$, forms small pale-yellow needles melting at 139·5°. The *amide*, $NO_2 \cdot C_{10}H_6 \cdot SO_2NH_2$, crystallises in long, slender, flexible needles which melt at 225°.

γ-Amidonaphthalenesulphonic acid, $NH_2 \cdot C_{10}H_6 \cdot SO_3H$, is prepared by reducing the nitro-acid with ferrous sulphate; it forms small, yellow, sparingly soluble needles.

When γ-nitronaphthalenesulphochloride is heated with an excess of phosphorus pentachloride, it yields the same dichloronaphthalene (m. p. 61°) which was previously obtained from the *ϑ*-acid.

N. H. M.

β-Naphthacridine. By J. H. Reed (*J. pr. Chem.* [2], **34**, 160).—*β-Naphthacridine*, $C_{10}H_6\langle \overset{-N-}{\underset{CH}{|}} \rangle C_{10}H_6$, is prepared by the action of methylal and acetone on *β*-naphthylamine in presence of hydrochloric acid. It separates from its solution in acetone in straw-coloured needles melting at 216°.

N. H. M.

Naphthanthraquinone and Naphthanthracene. By K. Elbs (*Ber.*, **19**, 2209—2212).—*Naphthanthraquinone*, $C_6H_4\langle \overset{CO}{CO} \rangle C_{10}H_6$, is readily obtained by the condensation of naphthoylbenzoic acid by means of sulphuric acid; the yield is 60 to 70 per cent. of the theoretical. It crystallises in lustrous, deep-yellow prisms, sparingly soluble in alcohol and ether, more soluble in chloroform, benzene and toluene, &c. It sublimes in needles and melts at 168°. It shows Liebermann's reaction when treated with zinc-dust and alkali; the colour produced is the same as in the case of anthraquinone. When an alcoholic solution is treated with sodium amalgam, the latter becomes surrounded with a dark violet zone from which red clouds rise; it is thus distinguished from anthraquinone which, under the same conditions, gives ultimately a green solution. The quinone does not yield a picrate. It is probably *α-β* naphthanthraquinone.

Naphthanthracene, $C_{18}H_{12}$, is prepared by warming the quinone with aqueous ammonia and zinc-dust, until the red colour of the liquid has

disappeared; the solution is poured off, the residue extracted with alcohol, the alcoholic solution treated with glacial acetic acid, and boiled for half an hour. On cooling, it separates in large plates with an intense greenish-yellow fluorescence. It melts at 141°. The *picrate*, $C_{18}H_{12}(C_6H_3N_3O_7)_2$, crystallises from benzene, toluene, &c., in red needles melting at 133°. It is readily decomposed by alcohol.

N. H. M.

Phellandrene. By L. Pesci (*Gazzetta*, **16**, 225—231).—The seeds of *Phellandrium aquaticum* contain about 2·5 per cent. of a terpene, $C_{10}H_{16}$, named by the author *phellandrene*. It is a liquid resembling geraniums in odour, soluble in alcohol, ether, and benzene. It boils at 171° under a pressure of 766 mm.; its sp. gr. at 10° is 0·856, and its specific rotatory power $[\alpha]_D = +17·64°$. It combines with hydrochloric acid to form a mixture of a monohydrochloride and a di-hydrochloride; heated for some time at its boiling point, it is converted into a polymeric modification, *diphellandrene*, $C_{20}H_{32}$, an amorphous, white substance, soluble in ether and chloroform; this melts at 86°, and is lævorotatory. *Nitrosonitrophellandrene*, obtained by the action of nitrous acid on the hydrocarbon, crystallises in long, silky needles melting at 94°, insoluble in the alcohols and petroleum, sparingly soluble in ether. It is lævorotatory, $[\alpha]_D = -183·5$; it gives Liebermann's reaction; on hydrogenation, it yields *phellandrenediamine*, $C_{10}H_{20}N_2$, and with ammonia, nitrophellandrene, $C_{10}H_{15}NO_2$, and an acid compound, $C_{10}H_{17}N_3O_4$. The *former* is a yellow liquid of marked aromatic odour, highly refractive, lævorotatory, and soluble in alcohol and chloroform; the *latter*, probably represented by the formula $NO_2{\cdot}C_{10}H_{16}(NO) : N(OH)$, crystallises in glistening needles, insoluble in water, sparingly soluble in alcohol and ether. On decomposition with concentrated hydrochloric acid, it yields hydroxylamine hydrochloride. Its *copper* salt crystallises in blue tables, and the lead salt in silky needles. *Amidophellandrene*, $C_{10}H_{15}{\cdot}NH_2$, is an oily, colourless liquid, of penetrating odour, sparingly soluble in water, soluble in alcohol and ether. It absorbs carbonic anhydride from the air to form a carbonate; its *sulphate* and *hydrochloride* crystallise in needles, and the *platinochloride* in yellow laminæ.

Phellandrenediamine, $C_{10}H_{16}(NH_2)_2$, is a colourless, thick liquid; it boils at 209—214°, and is very soluble in water and alcohol; its salts are very deliquescent, and its platinochloride crystallises in large, sparingly soluble, monoclinic prisms.

V. H. V.

Pimaric Acids. By A. Vesterberg (*Ber.*, **19**, 2167—2175; compare this vol., p. 365).—Dextropimaric acid, $C_{20}H_{30}O_2$ (*loc. cit.*), is obtained by treating French galipot with dilute alcohol and dissolving the white mass so obtained in hot 3 per cent. soda solution. After some days the sodium salt separates, and is purified by recrystallisation. The free acid is then liberated and crystallised from alcohol until it melts at 210—211°. The mother-liquor contains β-pimaric acid. The yield is $1\frac{1}{2}$ to 2 per cent. It crystallises in plates, probably rhombic; $a : b : c = 0·70564 : 1 : 1·89365$. The *potassium salt* crystallises in very slender needles; the *sodium* (with 5 mols. H_2O), *silver*, *barium* (with 9 mols. H_2O), and other *salts* are described.

The alkali salts are readily soluble in water, the other salts are insoluble in water and sparingly or not at all soluble in alcohol. The ethyl salt crystallises in flat prisms readily soluble in alcohol, ether, and benzene; it melts at 52°. The *methyl salt* melts at 69°. *Dextropimaric chloride*, $C_{20}H_{29}OCl$, is prepared by treating a solution of the acid in carbon bisulphide with phosphorus pentachloride. The crystalline residue obtained after distilling off the carbon bisulphide under diminished pressure is pressed and dried in a vacuum. It is very readily soluble in the usual solvents, and melts at 64—66°.

Dextropimaric acid distils in a vacuum almost entirely unchanged and without formation of sylvic acid (compare Laurent, *Annalen*, **68**, 335, and Duvernoy, *Annalen*, **148**, 143).

Dilute mineral acids have no apparent action on dextropimaric acid, alcoholic solution of hydrogen chloride acts only slightly on it. When an ethereal solution of the acid is saturated with hydrogen chloride and allowed to become warm, an isomeric acid, possibly sylvic acid, is formed, together with a small amount of a chlorinated compound.

When dextropimaric acid is heated with hydriodic acid and amorphous phosphorus, *colophene dihydride*, $C_{20}H_{34}$, is formed; it boils at 320—330° (uncorr.), and is scarcely attacked by boiling concentrated nitric acid. A very similar hydrocarbon, $C_{20}H_{32}$, was obtained by Montgolfier and Letts (Abstr., 1880, 669) by heating turpentine hydrochloride with sodium. The hydrocarbon obtained by Liebermann and by Haller from sylvic and "pimaric acid," appears to be a mixture of colophene and colophene dihydride (Abstr., 1885, 1241). N. H. M.

Nitrocamphor and its Derivatives. By P. Cazeneuve (*Compt. rend.*, **103**, 275—277).—When chloronitrocamphor is treated with zinc, copper, iron, or alkalis in presence of aqueous alcohol, it yields an oxide and chloride of the metal, or a chloride and chlorate of the alkali, whilst a true salt of the nitrocamphor, $NO_2C_{10}H_{14}MO$, is formed, and from this the nitrocamphor can be obtained by the action of hydrochloric acid.

25 grams of chloronitrocamphor are heated for half an hour with 250 grams of alcohol of 85° and an excess of granulated zinc-copper couple. The dark-brown liquid is agitated with zinc to precipitate the copper, evaporated to dryness on the water-bath, and treated with ether to remove any unaltered chloronitrocamphor. The zinc compound is left as a white powder, which may be purified by recrystallisation from alcohol, and is decomposed by adding hydrochloric acid to the alcoholic solution, which is then poured into water. In this way the nitrocamphor is precipitated as a soft, white solid, which softens at 97°, boils with decomposition at about 150°, and dissolves in alcohol, chloroform, ether and benzene. It does not crystallise from its solutions, and is waxy after fusion, but if kept for some months it becomes crystalline. Its rotatory power as determined from the benzene solution is $[\alpha]_j = -18{\cdot}7°$, and is similar to that of bromonitro- or chloronitro-camphor. The metallic compounds, however, are strongly dextrogyrate. The zinc compound has a dextrorotatory power $[\alpha]_j = +275°$. It is formed in accordance with the equation

$2NO_2{\cdot}C_{10}H_{14}ClO + Zn_3 + H_2O = (NO_2{\cdot}C_{10}H_{14}O)_2Zn + ZnO + ZnCl_2 + H_2$. The presence of water is essential; the reaction does not take place in absolute alcohol. The reactions with copper and iron are strictly analogous to that with zinc.

Nitrocamphor is a true acid, reddens litmus, decomposes carbonates, and yields definite compounds with metals. The zinc compound crystallises from alcohol in large, hexagonal tables which belong to the rhombic system. The ferrous salt forms garnet-red, hexagonal tables, and the copper salt crystallises in green needles. When a solution of the zinc salt in aqueous alcohol is treated with alkaline carbonates, it yields the alkaline salts, which crystallise readily. Silver nitrate added to the solution precipitates the silver salt in small, white needles, which alter when exposed to light. If the silver salt is treated with methyl or ethyl iodide it yields methyl- or ethyl-nitrocamphor. The ammonium salt does not crystallise, but if calcium chloride is added to its solution a crystalline precipitate of the calcium salt is formed. C. H. B.

Camphol from Valerian. By A. Haller (*Compt. rend.*, **103**, 151—153).—Oil of valerian boiling at 220—250° was heated for several hours with alcoholic potash, and the product poured into water. The precipitated camphol was washed with water, sublimed from lime, and repeatedly crystallised from light petroleum. The product crystallises in very friable, transparent, hexagonal tables, with a pungent, camphoraceous odour. It melts at 208·8°, and its solution in toluene has a rotatory power $[\alpha]_D = -37{\cdot}77°$. The corresponding camphor melts at 178·2°, rotatory power $[\alpha]_D = -42{\cdot}96°$; the monobromocamphor melts at 75·2°, rotatory power $[\alpha]_D = -127{\cdot}57°$, and the camphoric acid melts at 186·2°, rotatory power $[\alpha]_D = -46{\cdot}16°$.

These values are identical with those obtained for camphol of N'gai and its derivatives (this vol., p. 890), and it follows that the two substances are identical. C. H. B.

Glucosides from Japanese Oleaceæ. By J. F. Eykman (*Rec. Trav. Chim.*, **5**, 127—140).—Several species of the Oleaceæ are used as febrifuges, not only in Europe, but also in Asia. In this paper, the extraction and properties of a glucoside obtained from Japanese species are described. The glucosides from the *Olea fragrans* and *Forsythia suspensa* are found to be identical with one another, and also in general properties, with exception of the melting point, with the glucoside philyrine, $C_{27}H_{34}O_{11}$, obtained from the *Philyria*. The compound $C_{26}H_{32}O_{11}$, thus obtained, crystallises in colourless, silky needles, sparingly soluble in cold, more readily in hot water, insoluble in ether and petroleum; its aqueous solution is not precipitated by lead acetate and other mineral salts. It is decomposed by acids into glucose and another substance of phenolic properties; this melts under water at 70°, is readily soluble in alcohol and ether, sparingly soluble in water, insoluble in petroleum. Its product of oxidation by chromic acid has the odour of vanillin, but has not been further examined. V. H. V.

Xanthophyllidrin. By L. Macchiati (*Gazzetta*, **16**, 231—234).—After allusion to the researches of Tschirch on the preparation of pure chlorophyll (Trans., 1884, 57), the author describes the preparation of a yellow colouring matter, *xanthophyllidrin*, obtained from leaves. The formation of a yellow solution has been observed by Kraus and others, but has not been further examined. If the wash water used for the chlorophyllane be concentrated, a black precipitate separates; after filtration, dilution of the filtrate, and repetition of the process, such a precipitate no longer forms, and the solution on evaporation deposits citron-yellow crystals belonging to the monoclinic system. These are insoluble in alcohol, ether, and benzene, sparingly soluble in glycerol, but very soluble in water. These properties serve to distinguish this compound from xanthophyll, which is very soluble in alcohol and ether, but only sparingly soluble in water. Xanthophyllidrine gives an absorption-spectrum between F and G. It has been extracted from the leaves of the *Euonymus japonicus* and of several other species of plants. V. H. V.

Fluorescent Principle of Hydrastis Canadensis. By F. B. Power (*Pharm. J. Trans.* [3], **16**, 1092—1094).—Recent experiments show that the fluorescence of solutions of hydrastine or of those obtained from *Hydrastis*, is due to an oxidation product of hydrastine which is not present in pure hydrastine. Simple exposure to the air is, however, sufficient to produce it in a solution of hydrastine.

D. A. L.

Pyrroline-derivatives. By O. Fischer and E. Hepp (*Ber.*, **19**, 2251—2259).—*Pyrrolineazobenzene*, $C_4NH_4{\cdot}N_2{\cdot}Ph$, is prepared by slowly adding the theoretical quantity of diazobenzene chloride to a solution of 10 grams of pyrroline in 500 grams of alcohol to which 25 grams of sodium acetate has been added. It crystallises in long, golden-yellow needles, melts at 62°, is sparingly soluble in water, readily in ether, alcohol, and light petroleum; it has basic properties and dissolves readily in dilute hydrochloric acid with a reddish-yellow colour. Reducing agents very readily decompose it. The platinochloride forms small, red needles.

Pyrrolinediazobenzene, $C_4NH_3(N_2Ph)_2$, is obtained by mixing together pyrroline (1 mol.) and diazobenzene chloride (2 mols.) in alkaline solution, or by the action of diazobenzene chloride and soda on pyrrolineazobenzene. It crystallises in reddish-brown plates, melts at 131°, and can be sublimed at a higher temperature, is nearly insoluble in water, sparingly soluble in alcohol, moderately in ether, and readily in benzene. It dissolves in concentrated sulphuric acid to a deep blue solution.

Methylpyrrolinediazobenzene, $C_4NH_2Me(N_2Ph)_2$, is obtained by boiling an alcoholic solution of the last compound with methyl iodide in a reflux apparatus; it crystallises in red plates and melts at 196°.

Pyrrolineazoparatoluene, $C_4NH_4{\cdot}N_2{\cdot}C_6H_4Me$, prepared in manner similar to the benzene-compound, crystallises in tufts of long, flat, yellow needles and melts at 82°. The *diazobenzene* compound,

$C_4NH_3(N_2C_7H_7)_2$, crystallises in red prisms of steel-blue lustre and melts at 179°.

Ethylpyrrolinediazoparatoluene, $C_4NH_2Et(N_2C_7H_7)_2$, crystallises in yellow needles and melts at 180°. *Ethylpyrrolineazoparatoluene*, $C_4NH_3Et{\cdot}N_2{\cdot}C_7H_7$, was prepared from ethylpyrroline; it forms thick red prisms and melts at 62°.

Pyrrolineazo-α-naphthalene, $C_4NH_4{\cdot}N_2{\cdot}C_{10}H_7$, forms reddish-yellow plates of pale violet lustre, melts at 103°, and is readily soluble in alcohol. The corresponding *β*-compound forms golden plates which melt at 101°. *Pyrrolinediazo-α-naphthalene*, $C_4NH_3(N_2{\cdot}C_{10}H_7)_2$, crystallises in needles of cantharidine-like lustre, soluble in alcohol to a deep yellowish-red liquid. The *β*-compound crystallises in reddish plates and melts at 228°.

Pyrrolineazobenzeneazo-β-naphthalene, $Ph{\cdot}N_2{\cdot}C_4NH_3{\cdot}N_2C_{10}H_7$, obtained by the action of pyrrolineazobenzene on an alkaline alcoholic solution of diazo-*β*-naphthalene, or of pyrrolineazo-*β*-naphthalene, on diazobenzene chloride, crystallises in red plates of bluish lustre and melts at 151°.

Pyrrolineazoparadimethamidobenzene, $C_{12}H_{14}N_4$, crystallises in plates of green lustre, melts at 159°, and forms two series of salts.

Phenylpyrrolineazobenzene, $C_4NH_3Ph{\cdot}N_2Ph$, crystallises in brown prisms or in long, thin, reddish-yellow needles of pale blue lustre, melts at 117°, and is moderately soluble in alcohol.

Ethylpyrrolineazo-β-naphthalene, $C_{16}H_{15}N_3$, crystallises in thick red tables and melts at 74°.

When *α*-carbopyrrolic acid in alkaline solution is treated with diazobenzene chloride, it yields pyrrolinediazobenzene and azoparatoluene, the carboxyl-group being eliminated.

By the action of diazobenzene chloride on *α*-*α*-dimethylpyrroline, a substance is obtained crystallising in reddish-yellow prisms and melting at 124°, which seems to be an azo-compound; its platinochloride crystallises in microscopic tufts of golden-yellow needles.

The author considers that in the di-compounds the azo-groups enter the pyrroline molecule symmetrically, most probably in the *α*-*α* position. A. J. G.

Reduction of Acetylpyrroline in Alkaline Solution. By M. Dennstedt and J. Zimmermann (*Ber.*, **19**, 2204—2206).—*Pyrrylmethylpinacone*, $C_4NH_4{\cdot}CMe(OH){\cdot}CMe(OH){\cdot}C_4NH_4$, is obtained by treating acetylpyrroline in quantities of 5 grams with 250 c.c. of water and sodium amalgam. The product is extracted with ether and the ethereal solution evaporated; an oil is obtained which after a long time yields crystals. These are crystallised from ether. It forms lustrous monoclinic prisms, $a : b : c = 0{\cdot}5029 : 1 : 0{\cdot}3984$, sparingly soluble in hot water, readily in alcohol, benzene, and light petroleum. The anhydrous substance melts at 120°.

The oil obtained in the preparation of this substance is probably pyrryl methyl carbinol, $OH{\cdot}CHMe{\cdot}C_4NH_4$. It boils with partial decomposition at 290—300°. The above experiments were made to obtain further evidence as to the ketonic nature of acetylpyrroline (compare Abstr., 1885, 378). N. H. M.

Action of Paraldehyde on Pyrroline. By M. Dennstedt and J. Zimmermann (*Ber.*, **19**, 2189—2200; compare this vol., p. 367).—*Ethylpyrroline*, C_4NH_4Et, is prepared by adding 12 grams of zinc chloride to a mixture of 50 grams of pyrroline and 50 grams paraldehyde; the reaction begins at once with development of heat. The product is afterwards boiled in a metal bath for some time and then fractionally distilled. 8 grams of a fraction boiling at 160—170° are obtained, and 2 grams boiling at 175—185°; from 50 to 60 per cent. of the pyrroline is recovered unchanged. The lower boiling fraction is dissolved in toluene, boiled with caustic potash, and the solid product extracted with ether. The ethereal solution is dried with potash, the ether distilled off, and the residue fractionally distilled. It then boils chiefly at 163—165°. It is a colourless oil which becomes brown to black when exposed to air and light. The *acetyl-derivative*, C_4NAcH_3Et, is prepared by boiling 20 grams of ethyl-pyrroline with 120 grams of acetic anhydride and 24 grams of sodium acetate for six to eight hours; the excess of acetic anhydride is distilled off under diminished pressure and the residue steam distilled; it is colourless, but quickly resinises when exposed to air, and boils at 220—230°.

An *isomeric acetyl-derivative* in which the acetyl-group is attached to carbon was found in the residue from the first acetyl-compound. It is a crystalline substance which melts at 47° and boils at 249—250°. Boiling alkali solution does not decompose it. A *silver*-derivative, C_4NAgH_2EtAc, was prepared. When the acetyl-compound is boiled with an equal amount of benzaldehyde and dilute alkali, the *compound* $C_4NH_3Et{\cdot}CH : CHPh$ is formed; this crystallises from alcohol in long yellow needles melting at 149—150°. The *silver-compound* forms a yellow voluminous precipitate.

Dimethylpyrroline (Weidel and Ciamician, *Ber.*, **13**, 78), which has the same boiling point as ethylpyrroline, yielded two *acetyl-derivatives*, the one boiling at 260—280°, and the other, a crystalline substance, melting at 83—85°.

When ethylpyrroline is heated with five times its volume of strong hydrochloric acid for two hours at 120—140°, a dark brown product is formed, which yields an oil having basic properties and a strong odour of pyridine. The *platinochloride*,

$$CHMe\begin{matrix}<\\\end{matrix}\begin{matrix}CH : CH\\CH : CH\end{matrix}\begin{matrix}>\\\end{matrix}NH,H_2PtCl_6,$$

crystallises in red needles very readily soluble in water. The formation of this compound makes it probable that ethylpyrroline has the constitution $NH\begin{matrix}<\\\end{matrix}\begin{matrix}CH : CH\\CH : CEt\end{matrix}\begin{matrix}>\\\end{matrix}$.

The two isomeric methylpyrrolines (Ciamician, *Ber.*, **14**, 1057) when heated with hydrochloric acid yielded products having a strong odour of pyridine. Analyses of the platinochlorides point to the formula $(C_5NH_7)_2,H_2PtCl_6$. N. H. M.

Condensation Product of Pyrroline with Acetone. By A. Baeyer (*Ber.*, **19**, 2184—2185).—When pyrroline (1 part) is

dissolved in pure acetone (10 parts) and treated with a drop of hydrochloric acid, the liquid becomes red and begins to boil in a few minutes. It is then quickly cooled and kept for some time from the air. A quantity of well-formed crystals separate which are washed with alcohol. The compound has the formula $C_{14}H_{16}N_2$. It melts at 291°, dissolves readily in ether, chloroform, and acetone, sparingly in alcohol. It is insoluble in potash and in cold hydrochloric acid, but becomes red when boiled with the latter. Nitric acid dissolves it, yielding a blood-red liquid. N. H. M.

Action of Phthalic Anhydride on Methylpyrrolines. By M. Dennstedt and J. Zimmermann (*Ber.*, **19**, 2000—2003).—When 5 grams of methylpyrroline (boiling at 142—143°) dissolved in three times the volume of glacial acetic acid is heated with 10 grams of phthalic anhydride for five hours at 200°, a semi-solid mass is obtained. This is evaporated to dryness and recrystallised from alcohol, from which it separates in long, reddish-brown needles. When heated, it sublimes in lemon-coloured, feathery needles; it melts at 215°, and dissolves readily in alcohol, rather readily in glacial acetic acid and in ether. Analyses point to the formula $C_{13}H_9NO_2$. When the solution in dilute potash solution is made acid and extracted with ether, the *acid* $C_{13}H_{11}NO$ is obtained. The latter forms lustrous colourless crystals which melt at 159°. It readily changes to the anhydride when heated. The *silver salt*, $C_{13}H_{10}NO_3Ag$, is a white crystalline powder.

An *isomeride* of the above compound is obtained in a similar manner from methylpyrroline boiling at 147—148°. When sublimed, it forms yellow needles, resembling the first compound; it softens at 151° and melts at 157°. The *free acid* is a colourless, crystalline substance melting at 170—172°. The *silver salt* is a white crystalline powder. N. H. M.

Action of Ammonium Salts on Glycerol. By L. Storch (*Ber.*, **19**, 2456—2459).—The close affinity of the pyridine with the quinoline bases would lead to the supposition that the former would be obtained from glycerol and ammonia or its derivatives by Skraup's synthetic method. It is here shown that if glycerol is heated with a 30—40 per cent. solution of ammonium sulphate and concentrated sulphuric acid at 200—230°, the resultant distillate contains pyridine, β-picoline, and lutidine, together with higher homologues. With ammonium phosphate, a precisely similar result was obtained; but experiments with alcoholic ammonia, ammonium oxalate, and ammonium chloride were unsuccessful. V. H. V.

Hydroxypyridine. By A. Feer and W. Koenigs (*Ber.*, **19**, 2432—2433).—It is here shown that the hydroxyquinolinic acid obtained from amidomethylcarbostyril (Abstr., 1885, 1235) is identical with that prepared by the fusion of quinolinic acid with potash by Koenigs and Korner. It is further proved that the hydroxypyridine obtained from this acid is identical with that from hydroxyquinolinic and hydroxynicotinic acids. The hydroxyl grouping is therefore in the 1. position. V. H. V.

Quinoline Synthesis. By E. Bornemann (*Ber.*, **19**, 2377—2378).—It has been observed by La Coste that whereas ortho- and para-nitraniline yield a nitroquinoline by Skraup's synthesis, yet meta-nitraniline gives phenanthroline under the same conditions (Abstr., 1883, 85 and 811). This reaction was considered characteristic of the meta-derivatives. It is here shown, however, that paranitraniline yields pseudophenanthroline, identical with the compound obtained by Skraup and Vortmann from paraphenylenediamine.

V. H. V.

Phenylquinaldinic Acid and Phenylquinoline. By W. Königs and J. U. Nef (*Ber.*, **19**, 2427—2432).—The close relationship of the hitherto unprepared phenylquinoline (Me : Ph = 2′ : 4′) with the cinchona alkaloïds on the one hand and papaverine on the other, gives special interest to its preparation. It is here shown that this compound may be obtained by the decomposition of phenylquinaldinic acid, obtained by the oxidation of phenylquinaldine (Abstr., 1885, 1236) through the phthalone.

Phenylquinaldinic acid, $C_9NH_5Ph{\cdot}COOH$ [COOH : Ph = 2′ : 4′] crystallises in golden needles melting at 171°, sparingly soluble in all neutral reagents; it forms salts both with acids and bases, of which the *sodium* and *potassium* salts crystallise in colourless needles, and the *platinochloride* in long, yellow needles. When heated at 180—190° it gives off the elements of carbonic anhydride, and is converted into *phenylquinoline*, C_9NH_6Ph [Ph = 4′]. This base forms crystalline flocks which melt at 61—62°; it dissolves in most menstrua with the exception of water. Its *sulphate* and *hydrochloride* are very soluble and display a violet fluorescence, the *chromate* and *platinochloride* crystallise in tables. In the course of the preparation of orthonitrodiphenylmethane from benzene and nitrobenzyl chloride in presence of aluminium chloride (*supra*), the formation in small quantities of a substance possessing all the properties of acridine was observed; the reaction is probably as follows:—

$$NH_2{\cdot}C_6H_4{\cdot}COPh - OH_2 = C_6H_4\begin{cases}CH\\ |\\ -N\end{cases}C_8H_4;$$

in presence of water no acridine is formed, but only aniline and benzoic acid, together with small quantities of subsidiary products.

V. H. V.

Diquinoline. By G. Jellinek (*Monatsh. Chem.*, **7**, 351—359).—Claus has described a diquinoline obtained by heating quinoline hydrochloride with aniline; the latter apparently plays no essential part in the reaction (Abstr., 1882, 214); it is considered identical with the compound described by Williams (Abstr., 1881, 613). As it seemed to be an open question whether the substance thus prepared was perfectly homogeneous, Claus' experiments were repeated; the hydrochloride of the base was frequently recrystallised from water and the base from xylene and alcohol; the purified base could be distilled and solidified, in the crystalline form. The analytical results, as also a vapour-density determination, showed that the composition of the base was that of an *amidophenylquinoline*, $C_{15}H_{12}N_2$, and not a

diquinoline, $C_{18}H_{14}N_2$. It forms aggregates of yellowish-white needles melting at 136·5°, insoluble in cold water, soluble in benzene, alcohol and chloroform. Its *hydrochloride* crystallises in delicate, colourless crystals, the *platinochloride* in small, crystalline plates, and the *methiodide* in minute needles melting at 220° with decomposition. The product of the oxidation of the base by potassium permanganate, although not minutely examined, contained neither a dipyridyl- nor a dipyridine-carboxylic acid, but probably quinolinic acid together with two other acids. V. H. V.

Action of Ethyl Acetoacetate and Ethyl Acetonedicarboxylate on Hydrazo-compounds. By H. v. Pechmann (*Ber.*, **19**, 2140—2142).—Referring to Müller's work (this vol., p. 899), the author claims priority in the synthesising of phenylmethoxyquinizine (this vol., p. 898), and maintains his own melting point of 122°, and the formation of anhydrous crystals, as against Müller's melting point 122°, and crystals containing $\frac{1}{2}OH_2$.

Hydrazotoluene and ethyl acetoacetate similarly form *tolylmethoxyquinizine*, yielding crystals melting at 143°, and showing Knorr's antipyrine reaction with ferric chloride.

With ethyl acetonedicarboxylate, hydrazotoluene yields *ethyl tolylmethoxyquinizinecarboxylate*. L. T. T.

Preparation of Quinoxalines. By A. Scheidel (*Dingl. polyt. J.*, **261**, 48).—Orthonitramidoparamethoxybenzene is obtained by heating 100 parts of nitrodimethylquinol, $C_6H_3NO_2(OMe)_2$, for six hours with 600 parts of aqueous or alcoholic ammonia in a closed vessel at 130—140°. The product is purified by solution in acid and reprecipitation by neutralising the solution with alkali. It crystallises from alcohol in plates resembling azobenzene in colour, melts at 125°, and forms paramethoxyorthophenylenediamine when reduced. The latter yields quinoxalines by condenation with glyoxal. D. B.

Ethylamidoacetocyamidine, a new Creatinine. By E. Duvillier (*Compt. rend.*, **103**, 211—213).—*Ethylamidoacetocyamidine*, $HN{\cdot}C<^{-NH{\cdot}CO-}_{NEt{\cdot}CH_2>}$, is obtained by mixing concentrated aqueous solutions of ethyglylcocine and cyanamide, and allowing the mixture to stand, when it deposits long needles, which can be purified by crystallisation from water. The purified crystals are anhydrous, flattened needles which often become lamellar; they dissolve in 11·5 parts of water at 25°, and in 96 parts of alcohol at the same temperature. The creatinine separates from the alcoholic solution in small prisms. The action of ethylglycocine on cyanamide yields a creatinine and not a creatine, and this result together with the author's previous researches leads to the following laws of the synthesis of creatinines and creatines:—

(1.) The action of cyanamide on amido-acids derived from ordinary ammonia yields creatines from which the corresponding creatinines can readily be obtained.

(2.) Amido-acids derived from methylamine yield creatinines, with the exception of methylglycocine and α-methylamidopropionic acid, which yield creatines.

(3.) Amido-acids from ethylamine all yield creatinines and no creatines.

It is evident that the general result of the action of cyanamide on amido-acids is the formation of the creatinines, and the cases in which creatines are produced form exceptions to the general rule.

C. H. B.

Behaviour of Morphine towards Potassium Chromate. By F. Ditzler (*Arch. Pharm.* [3], **24**, 701—705).—The various methods of estimating morphine in opium are more or less unsatisfactory, and the author's attempt to found one on the reactions between this alkaloïd and potassium chromate has not led to any better results. Morphine salts in solution, shaken with excess of potassium chromate solution, give a precipitate of morphine, whilst morphine chromate is precipitated when only very small quantities of potassium chromate are gradually added. Morphine chromate attaches itself to the walls of the precipitating vessel in the form of light-yellow needles of the formula $(C_{17}H_{19}NO_3)_2,H_2CrO_4$. J. T.

Pseudomorphine. By O. Hesse (*Annalen*, **234**, 253—256).—Pseudomorphine and diacetopseudomorphine exhibit the following characteristic reactions. When the substance is mixed with an equal weight of cane-sugar, and dissolved in pure sulphuric acid, a dark-green coloration is produced which gradually turns brown. If the acid contains a minute quantity of a ferric salt, a blue coloration turning dark-green is produced. Under these conditions, morphine gives a violet-red coloration. W. C. W.

Specific Gravity of Crystalline Strychnine. By T. P. Blunt (*Pharm. J. Trans.* [3], **17**, 62).—A crystal of strychnine remained suspended in a solution of lead acetate, sp. gr. 1·13, which was therefore the sp. gr. of the crystal also. D. A. L.

Strychnine Citrate. By F. H. Fischedick (*Pharm. J. Trans.*, [3], **17**, 170—171).—When strychnine, even in excess, is digested with a hot solution of citric acid, distrychnine citrate is produced, which crystallises in two forms. In one form, $(C_{21}H_{22}N_2O_2)_2,C_6H_3O_7,4H_2O$, the crystals are thin, transparent, micaceous plates with pearly lustre; at 15° one part of this salt dissolves in 45·5 of water or 114·83 parts of alcohol. The other form contains only 2 mols. H_2O, and the crystals are needle-shaped, radiating from a point to form silver-white cones. Both salts yield acid solutions. An attempt to prepare tristrychnine citrate by allowing a chloroform solution of strychnine mixed in proper proportions with an alcoholic solution of nitric acid to evaporate spontaneously, resulted in the production of a granular residue; this when treated with hot water yielded pure strychnine and the needle-like crystals of distrychnine citrate. Strychnine citrate of commerce is a white, amorphous powder, and behaves in a similar manner to the above granular mixture. D. A. L.

Reactions of Pilocarpine. By E. Hardy and G. Calmels (*Compt. rend.*, **103**, 277—280).—When barium β-pyridinelactate is distilled, it yields *hydroxyethylpyridine*, $C_5NH_4{\cdot}CHMe{\cdot}OH$, a viscous liquid which is miscible with alcohol and water, and is not removed from its aqueous solution by ether. With platinum chloride it yields a brownish-yellow precipitate, $PtCl_4(C_7H_9NO)_2$, which dissolves in hydrochloric acid, and if this solution is evaporated, it leaves a gummy residue from which the acid salt crystallises in needles and lamellæ. When heated with gold chloride, hydroxyethylpyridine yields a metallic mirror; if the solution is now mixed with platinum chloride, it gives a bulky pale-yellow precipitate of the compound $H_2PtCl_6(C_7H_{17}NO + H_2O)_2$, which is the platinochloride of methylcarboxy-β-pyridine, identical with that obtained by synthesis. Hydroxyethylpyridine hydrochloride becomes brown when its solution is evaporated with exposure to air, and is converted into β-pyridinecarboxylic acid. These reactions complete the proof that pilocarpine is an α-hydroxy-derivative of β-pyridinelactic acid.

If the barium-derivative of pilocarpine or pilocarpidine is distilled, it yields a liquid which has a peculiar odour, and forms a very deliquescent, crystalline hydrochloride and nitrate. When gold chloride and platinum chloride are added to the aqueous solution of this liquid, they yield respectively the compounds $AuCl_3,C_9H_{14}N_2$, $AuCl_3,HCl,C_9H_{14}N_2$, $PtCl_4,(C_9H_{14}N_2)_2$, and $H_2PtCl_6,(C_9H_{14}N_2)_2$, amorphous precipitates which agglomerate in warm water or aqueous alcohol, and are very soluble in alcohol. The composition of these salts shows that the base is univalent, so that jaborine is not analogous to sparteine. Jaborine has the constitution

$C_5NH_4{\cdot}CHMe{\cdot}NMe_2$. C. H. B.

Ulexine. By A. W. Gerrard (*Pharm. J. Trans.* [3], **17**, 101 and 229—230).—*Ulexine* is an organic base discovered by the author in *Ulex europæus*. The crushed seed is exhausted by percolation with 84 per cent. alcohol, and the residue, after distilling off the alcohol, is shaken with successive large volumes of dilute hydrochloric acid (1 : 1000). This solution is neutralised with sodium carbonate, filtered, concentrated by evaporation, the resin allowed to subside, and the solution treated with excess of soda and extracted with chloroform. The chloroform extract is agitated with dilute hydrochloric acid, and on evaporating the hydrochloric solution, ulexine hydrochloride crystallises out. This salt is purified by recrystallisation, and the free base obtained from it by treatment with soda and chloroform. Ulexine forms colourless odourless, crystals, with a bitter and somewhat pungent taste; it is freely soluble in water, forming a strongly alkaline solution, and is insoluble in ether. When heated it fuses, darkens and decomposes, giving off vapour which burns with a yellow, smoky flame and leaves no residue. It forms well crystallised salts with hydrochloric, hydrobromic, nitric, sulphuric, and oxalic acids, all soluble in water; very strong solutions yield precipitates with soda, but not with ammonia. The platinochloride crystallises readily from aqueous solutions. Picric acid gives a yellow precipitate, potassium permanganate is almost immediately

reduced. The aqueous solution of the pure base gives a green precipitate with ferrous sulphate, a black one with mercurous nitrate, and a white precipitate with mercuric chloride. A characteristic deep red colour is obtained when a particle of a ulexine salt is moistened with a drop of ferric chloride. The bark and young tops of furze contain ulexine, but in much less quantity than the seeds, which when treated in the manner described above yielded 0·191 per cent. of this base. Ulexine causes clonic spasms in frogs, and when the chloride is placed on the tongue it produces local numbness, similar to but not so powerful as that produced by cocaïne.

D. A. L.

Poison of the Tetrodon. By J. T. Eykman (*Rec. Trav. Chim.*, **5**, 140—149).—The Japanese Government have issued cautions against the consumption of a certain species of fish, the tetrodon (in Japanese, *tugu*), the spawn and various organs of which produce toxical effects resembling those of curari; several deaths are registered yearly from this cause. An account is given of attempts to isolate the specific toxical substance, and of an examination of its effects. Inasmuch as it is obtained from the organs of the fish when fresh, it is most probably not a product of putrefaction, but rather of the metamorphosis by oxidation of albumin, and is thus analogous to the bases of the oxyethylenic series. It is extracted from the spawn by heating it with water at 65—70°, adding lead acetate solution and a few drops of acetic acid. The filtrate from the precipitate at first formed becomes turbid on standing, and the addition of ammonia produces a flocculent precipitate. This is redissolved in water, decomposed by hydrogen sulphide, and the solution precipitated with alcohol. Thus prepared it is a white, amorphous, hygroscopic powder, insoluble in ether, chloroform, and petroleum. Its aqueous solution gives none of the more general reactions of the alkaloïds; heated with sodium it gives the cyanogen reaction. Elementary analysis points to a provisional formula $C_{18}H_{32}N_2O_{13}$, which corresponds with that of a diamine of a polysaccharide. In its composition, properties, as also in its mode of separation by lead acetate, it resembles ergotic acid.

V. H. V.

Supposed Ptomaïnes of Cholera. By V. Oliveri (*Gazzetta*, **16**, 256—262).—As a general outcome of recent researches on the ptomaïnes or putrefaction alkaloïds, it has been proved that these substances are not pre-existent in pathological preparations, but owe their origin to the action of acids used in the processes of extraction (Abstr., 1885, 278). Recently, however, it has been stated that such alkaloïds can be obtained from the evacuations and blood of patients suffering from cholera, and also in the cultivation of Koch's comma bacillus (Abstr., 1885, 404). Comparative experiments were made with these cultivations either by themselves or infected with the intestinal contents of a subject who died of malignant cholera, or with the micro-organisms of water. In the one case the cultivations and liquids used for extraction were kept carefully alkaline, and no formation of alkaloïds was observed; in the other it was found that the most dilute acids, even without the application of heat, cause the production of these substances, from the decomposition of the lecithin

and proteïds present in the preparations. It is moreover probable that skalote and hydrogen sulphide are exclusively products of decomposition of certain species of bacteria in potable waters.

V. H. V.

Blood Proteïds of Lower Vertebrata. By W. D. Halliburton (*J. Physiol.*, **7**, 319—323).—The following are the conclusions drawn from the examination of the blood of types of the different classes of the animal kingdom:—

1. That the proteïds in the blood of birds resemble those of other warm-blooded animals or mammals.

2. That the proteïds in the blood serum of cold-blooded animals differ from those in warm-blooded animals in these particulars:—(*a.*) The percentage of total proteïds is smaller. (*b.*) The serum albumin is especially diminished, not only absolutely but relatively, to the serum globulin present. This is illustrated by examples selected in the following table:—

	Proteïds in the blood serum.		
Animal.	Total proteïds per cent.	Serum globulin.	Serum albumin.
Man	7·62	3·10	4·52
Rabbit	6·21	1·78	4·43
Pigeon	5·01	1·32	3·69
Frog	2·54	2·18	0·36
Newt	3·74	3·31	0·43
Dogfish	1·62	1·17	0·45

(*c.*) The serum albumin seems to be a single proteïd in cold-blooded animals, and cannot be differentiated into three by fractional heat coagulation, as in birds and mammals.

3. In all the vertebrates examined, the globulins of the blood, fibrinogen and serum globulin possess the same properties.

W. D. H.

Colouring Matter of Serum. By W. D. Halliburton (*J. Physiol.*, **7**, 324—326).—The blood serum of the pigeon, hen, dove, and tortoise is of an orange-red colour. This is due to the presence of a yellow lipochrome (*Serum luteïn*), which can be most readily extracted by means of ethyl alcohol. It gives the ordinary colour tests for lipochromes, and is soluble in alcohol, ether, chloroform, benzene, carbon bisulphide, and light petroleum, insoluble in turpentine. It is bleached by sunlight; oxidising and reducing agents have no effect on it. It gives spectroscopically a band from λ475 to λ500. It differs spectroscopically and in its solubilities from the lipochrome described by Krukenberg (*Sitzungsber. Jena. Gesell. Med.*, 1885), as occurring in the serum of the ox.

It is identical with the colouring matter of the fat of these same animals; it can also be extracted from the muscles of the pigeon and those of the lower limb of the hen: this is due to the fact revealed by microscopic examination, of the existence of a large amount of fat mixed with the muscular fibres in those situations. W. D. H.

Pepsinogen and Pepsin. By J. N. Langley and J. S. Edkins (*Proc. Physiol. Soc.*, 1886, 15—16).—The object of the experiments was to discover a method of determining the relative amounts of pepsin and pepsinogen in any given fluid, and thence to determine whether both exist in the gastric glands. The following two methods give approximate results:—(1.) This depends on the power of sodium carbonate to destroy pepsin being much greater than its power to destroy pepsinogen. Thus if equal volumes of neutralised acid extract of gastric mucous membrane, and 1 per cent. sodium carbonate solution are mixed, $\frac{9}{10}$ to $\frac{19}{20}$ of the pepsin is destroyed in 15 seconds. (2.) This depends on the power of carbonic anhydride to destroy pepsinogen being greater than its power to destroy pepsin. If an aqueous extract of a frog's œsophagus be taken, and a stream of carbonic anhydride passed through it for half an hour, $\frac{19}{20}$ to $\frac{59}{60}$ of the digestive power of the fluid is destroyed; whilst if an aqueous extract be warmed with dilute acid, neutralised, and then the gas be passed through it; there is little or no loss of digestive power. This destruction of pepsinogen by carbonic anhydride is lessened by very small amounts of peptone. The passage of carbonic anhydride through the aqueous extract produces a precipitate of globulins; but pepsinogen is not carried down with this unaltered, since the precipitate dissolves in dilute hydrochloric acid, and the solution so formed has very slight digestive power. Pepsinogen and pepsin are both destroyed at 54—57°, the temperature at which the globulins coagulate. The destruction of pepsinogen by carbonic anhydride is increased by the presence of a small amount of neutral salt. Oxygen does not convert pepsinogen into pepsin. Carbonic oxide has no effect on either pepsin or pepsinogen. On applying the above methods to the œsophageal glands of the frog, it is found that little or no pepsin is present in the cells there. W. D. H.

Preparation of Peptone. By E. Merck (*Dingt. polyt. J.*, **261**, 316).—The author calls "nucleo-proteïds" substances which, when boiled with water under pressure or treated with acids, alkalis, or ferments, are resolved into nucleïn and albumin, for instance, the vitellin of the yolk of eggs or the caseïn of milk. To prepare peptone from these substances 100 grams of caseïn are treated with 1 litre of distilled water at 150—170° for about 10 hours. The mixture is then filtered, and the solution containing the peptone again heated with water in order to separate additional quantities of unaltered albumin remaining in the solution. The final filtrate contains caseïn-peptone, which is separated in the usual manner. Another process consists in treating the nucleo-proteïds with a 0·1 per cent. solution of sodium hydroxide at 80—90° for about eight hours, neutralising with acid, filtering and separating the peptone. D. B.

Caseïn-peptone. By H. Thierfelder (*Zeit. physiol. Chem.*, **10**, 577—588).—Caseïn prepared from milk by the author, and "caseïn puriss" (Merck), were subjected to gastric digestion. The ultimate product, peptone, and the intermediate products were submitted to elementary analysis. The intermediate products, two in number, are

designated propeptone I and II. Propeptone I, precipitated by sodium chloride from the neutralised products of digestion, contains three substances, which correspond with the proto-, hetero-, and dysalbumose of Kühne and Chittenden. From the filtrate, propeptone II is precipitated by hydrochloric acid; this appears to be a single substance, its solution is rendered cloudy by acetic acid and ferrocyanide of potassium, is not coloured by nitric acid, and gives the biuret reaction. After the separation of the propeptones, peptone remains in solution and can be precipitated therefrom by phosphotungstic acid. W. D. H.

Compounds of Hæmatin. By V. D. Harris (*Brit. Med. J.*, 1886, **2**, 103—104).—Iodine and bromine compounds of hæmatin exist that are allied to hæmin. They are formed either by allowing iodine or bromine vapour to pass through an ethereal solution of hæmatin; or better, by allowing the halogens to come into contact with hæmatin in a nascent state, that is, by mixing the potassium salt with glacial acetic acid, and boiling with a solution of hæmatin. In physical and spectroscopic properties these compounds very closely resemble hæmin. W. D. H.

Physiological Chemistry.

Action of the Pulmonary Tissue in the Expiration of Carbonic Anhydride. By L. Garnier (*Compt. rend.*, **103**, 280—281).—Pulmonary tissue contains an acid substance which is distinct from taurine, and may or may not be identical with Verdeil's pneumic acid. This acid may play an important part in the expiration of carbonic anhydride from the lungs by acting on the carbonates in venous blood. C. H. B.

Gastric Digestion during Deprivation of Chlorine. By A. Cahn (*Zeit. physiol. Chem.*, **10**, 522—535).—It is well known that on a diet containing no chlorine (powdered meat thoroughly washed free from chlorides by means of distilled water), the chlorides disappear from the urine. Observations on the gastric juice of dogs fed on such diet, showed that secretion to be then free from hydrochloric acid, no other acid taking its place. The secretion of pepsin, however, continues, and becomes active when dilute hydrochloric acid is added to the neutral gastric juice. A small amount of chloride is, however, present; this is probably due to some hydrochloric acid being formed and uniting with the ammonia produced by putrefactive processes in the stomach, to form ammonium chloride. When putrefaction is prevented by pepper, chlorides are still found united to fixed alkalis. When carbohydrates are administered with the washed meat, lactic acid is formed, and so peptonisation occurs in the stomach. When excess of chlorides are present in the organism, an abundant secretion of hydrochloric acid begins immediately. W. D. H.

Gastric Juice in Acute Phosphorus Poisoning. By A. Cahn (*Zeit. physiol. Chem.*, **10**, 517—521).—Acute phosphorus poisoning produces intense fatty degeneration of the mucous membrane of the stomach. In spite of this, it is found in the dog that the gastric juice still contains active pepsin and the normal amount of hydrochloric acid. Sarcolactic acid is also present; this is in accordance with the well-known fact that in phosphorus poisoning the blood is overladen with abnormal acid products, which find their way into the urine, and it would now seem into the gastric secretion also. These observations may throw light on digestive processes in man during attacks of fever, a certain amount of fatty degeneration of gland cells being then present. W. D. H.

The Estimation of the Nitrogen in Products of Metabolism. T. Pfeiffer (*Zeit. physiol. Chem.*, **10**, 561—576).—The author has previously criticised Stutzer's method of investigation of this subject (this vol., pp. 377, 571). He now supports his position by experiments on pigs, in which he contrasts the results obtained by the method of natural digestion with those obtained by Stutzer's method of artificial digestion. Stutzer found that for every 100 grams of dry food material 0·4 gram of nitrogen passed off in products of metabolism; the author obtains an average number nearly twice as great.
W. D. H.

Digestion in Rhizopods. By M. Greenwood (*J. physiol.*, **7**, 253—273).—Amœba and actinosphærium were the animals observed. Starch is not digested by either animal; fat globules are not digested by amœba, a slow digestion of them probably occurs in actinosphærium. Nitrogenous food is digested, not by direct contact with the acting protoplasm, but by something passed out by the protoplasm into the vacuole of digestion. This secretion is probably not acid, but its formation is not excited by such innutritious material as litmus; the methyl-violet and tropæolin tests were unsuccessful. W. D. H.

Nutritive Value of Edible Fungi. C. T. Mörner (*Zeit. physiol. Chem.*, **10**, 503—516). A large number of edible mushrooms of various kinds gathered in Sweden were submitted to the following analyses, the results of which are given in complete tables:—(1) Total nitrogen; (2) proportion of proteïd nitrogen to extractive nitrogen; this analysis was founded on the fact that the proteïds of the dry powdered fungi were insoluble, the extractives soluble in 80 per cent. alcohol; (3) artificial digestion experiments; the proteïds were submitted to gastric digestion, the residue to pancreatic digestion; the final residue weighed and analysed. The proportion of digestible to indigestible proteïds was thus found. The average percentage of proteïd present was found to be 15·7 of dry material, of which over half (8·7 per cent.) was digestible. The nitrogenous value of these fungi is therefore very near that of cabbages, which contain on an average 13·3 per cent. of proteïd (Böhmer; *Landw. Versuchs-Stat.*, **28**, 247). W. D. H.

Digestibility of Fresh and Dried Beet-residues. By T. PFEIFFER and F. LEHMAN (*Bied. Centr.*, 1886, 537—539).—Sliced beet from the diffusion process was employed as fodder for two sheep; during one period, they were fed with it in the damp state, and for another equal period with it in the dry state, the total solid matter being the same in quantity; during both periods, they received extra fodder of hay, wheat-chaff, and earthnut cake; the results show that the dried residue is quite as digestible as the fresh, and is of equal nutritive value. J. F.

Presence of Iron in the Liver. By S. S. ZALESKI (*Zeit. physiol. Chem.*, **10**, 453—502).—All observations hitherto made on the amount of iron in the liver have been made when the organ has contained blood, and are therefore of but little value. The liver can be obtained perfectly free from blood by thoroughly washing it out from the vessels by means of a 2·5 per cent. cane-sugar solution; this solution does not alter the liver cells, either macroscopically or microscopically. Iron is found to be a constant constituent of liver tissue; its quantity, however, varies within wide limits. It is found in all the morphological constituents of the liver tissue in organic combinations, both with albuminates and with nucleïn. In the iron-nucleïn group of compounds, one is present which gives the ordinary tests for iron in contradistinction to the others which do not; from this latter group one compound, *hepatin*, has been isolated as follows:—The liver cells are first extracted with 75 per cent. sodium chloride solution, the residue submitted to artificial gastric digestion to remove proteïds; the residue is extracted with ether to remove pigment, fat, &c., dissolved in ammonia, and precipitated by alcohol. The iron in these compounds is present in at least two, probably in three, states of oxidation, in the ferrous, ferric, and ferrosoferric states. In all cases oxide was found, ferrous in 52 per cent. Phosphoric acid in 40 per cent. of the livers analysed was not present in sufficient amount to combine with all the iron. The amount of dry residue of the liver varies, like the iron, within wide limits. Proteïds precipitable by carbonic anhydride are not present in the liver. In the microscopical investigation of the liver, the momentary contact of the tissue with the clean steel of the section cutter does not influence the microchemical reactions. Of all the macrochemical reactions the most delicate is that with potassium thiocyanate and hydrochloric acid, or with potassium ferro- or ferri-cyanide and hydrochloric acid; this latter test is also the best adapted for microscopical investigation.
W. D. H.

Influence of Strychnine and Curare on the Glycogen of the Liver and Muscle. By B. DEMANT (*Zeit. physiol. Chem.*, **10**, 441—452).—In each experiment, two animals (rabbits or new-born dogs) were killed; one by the poison, the other by bleeding. The amount of glycogen in the liver and muscles of the two animals was then estimated, and it was found that the glycogen in the organs of the animal killed either by strychnine or curare, was diminished greatly, often to the merest trace in both the liver and the muscles. The

urine of animals killed by strychnine contained no sugar, but in that of those killed by curare, sugar was always present.

In new-born dogs, the lethal dose of strychnine is greater than in adults, but a small dose which produces no convulsions causes a great diminution of the glycogen contained in the organs mentioned.

W. D. H.

Liquid from a Cyst. By P. Macquaire (*J. Pharm.* [5], **13**, 222—224).—The liquid was taken from the *inguino-abdominal* region of a man 32 years of age. The total amount was 268 c.c. On allowing it to remain in a flask for some days, it separated into two distinct layers; the upper layer was yellow by transmitted, and green by reflected light, slightly odorous, viscous, and of a syrupy consistence; its reaction was alkaline, and when dried at the ordinary temperature gave a translucent residue. The lower layer was greenish-white, and apparently consisted of a fibrinous coagulum, enclosing a large number of pus globules visible under the microscope. The whole was thrown on a filter, and the filtrate had a sp. gr. of 1·0199 at 0°, and gave a solid residue of 7·9 per cent. and an ash of 0·37 per cent. Dilute acetic acid added drop by drop to the filtrate throws down a white precipitate, insoluble in slight excess of the reagent, but soluble in a large excess of pure acetic acid. The acidified liquid, separated from the white precipitate, forms a gelatin-like disc on its surface when heated on the water-bath. The original filtrate, diluted with 10 volumes of water and treated with a current of carbonic anhydride, gave an abundant precipitate of *paraglobulin* and *fibrinogen*. The filtrate from this precipitate gives no precipitate with dilute acetic or nitric acid; but concentrated nitric acid gives an abundant precipitate of albuminoïd matter, which is promptly coloured yellow, probably by the transformation of a small quantity of this substance into xanthoproteic acid. Dilute aqueous soda redissolves the precipitate, and the solution, although limpid, retains the yellow colour. The original liquid, diluted with water and treated with nitric acid containing nitrous acid, gives the characteristic green coloration produced by the colouring matter of bile; this liquid was found to have the composition:—Water, 92·100; paraglobulin, 2·030; fibrinogen, 1·373; albumin coagulated by heat, 0·684; albumin coagulated by nitric acid only, 3·775; mineral constituents, 0·038 per cent. Hence the albuminoïd matter amounted to 7·862 per cent., including under this term several products which present the general characters of such matter.

J. T.

Composition of Suint. By E. Maumené (*Compt. rend.*, **103**, 350—352).—The author confirms Buisine's results (this vol., p. 902). The products of the pyrogenic decomposition of that portion of the suint which dissolves in water are extremely complicated. Alkaline substances are removed by means of dilute sulphuric acid, and acids by treatment with concentrated aqueous potash. The liquid then contains ethyl ether mixed with ethyl alcohol and analogous compounds, ketones, &c. This is the first case in which ether has been found amongst the products of pyrogenic decomposition.

C. H. B.

The Precipitate produced by Picric Acid in Normal Urine. By M. JAFFE (*Zeit. physiol. Chem.*, **10**, 391—400).—With human urine, the addition of a concentrated solution of picric acid produces in the course of an hour a small amount of crystalline sediment. On treating this precipitate with hot water, two substances can be separated from it: one insoluble in hot water, uric acid; the other, comprising the greater part of the sediment, soluble in hot water; the latter is a double salt of creatinine picrate with potassium picrate, having the formula $C_4H_7N_2O,C_6H_3O(NO_2)_3 + KC_6H_2O(NO_2)_3$. It crystallises in lemon-coloured needles or thin prisms, is readily soluble in hot alcohol, sparingly in cold alcohol, and almost insoluble in ether. It contains no water of crystallisation, and detonates when heated. Besides these two substances, there are others present in smaller quantities which have not yet been investigated. With dog's urine, the precipitate obtained with picric acid contains little or no uric acid. The kynurenic acid of dog's urine is not precipitated.

Creatinine picrate, $C_4H_7N_3O,C_6H_3O(NO_2)_3$, is formed when solutions of picric acid and creatinine are mixed; after being recrystallised from hot water, it forms thin, yellow, lustrous needles; it is free from water of crystallisation, and detonates on heating. It is more easily soluble in water than the double salt above mentioned. *Creatinine kynurenate*, formed by adding powdered kynurenic acid to a hot dilute solution of pure creatinine, crystallises in bundles of colourless thin prisms, which are easily soluble in water, but decompose when the water is heated with formation of kynurenic acid.

When a solution of picric acid is added to a solution of creatinine with a drop of dilute potash or soda, a deep red colour is produced even when the dilution of the creatinine is 1 : 5000. This is a delicate test, and by it the presence of creatinine can be shown in the urine of man, dog, and rabbit. Acetone gives a similar but not so intense a colour in the cold; dextrose gives the colour only after heating.

W. D. H.

Lipaciduria. By R. v. JAKSCH (*Zeit. physiol. Chem.*, **10**, 536—560) —Observations on the occurrence of fatty acids in the urine of healthy and diseased persons led to the following results:—

1. In normal urine, traces of fatty acids occur, the highest amount being 0·008 gram per diem, and the acids present are formic and acetic.

2. On treating normal urine with oxidising agents, from 0·90—1·5 grams of fatty acids can be obtained from the day's total secretion, the acids present being formic, acetic, and probably also butyric and propionic.

3. In febrile conditions, 0·06 gram of these acids may be secreted per diem; in lipaciduria due to liver disease as much as 0·6 gram may be present in the day's total urine. As with healthy urine, this quantity is much increased by previous treatment with oxidising agents.

W. D. H.

Uric Acid in Insects and Molluscs. By C. A. MACMUNN (*J. Physiol.*, **7**, 128—129).—Griffiths (*Chem. News*, **51**) has described uric acid in the green gland of the cray-fish, and in the organ of

Bojanus of the mussel. The present research shows that uric acid can be obtained from the renal organs of other invertebrate animals, namely, an insect, *Periplaneta orientalis*, and from the pulmonate molluscs *Helix* and *Limax*. The organs suspected to contain uric acid were crushed, boiled with distilled water, the extract evaporated to dryness, washed with hot alcohol, and again dissolved in boiling water and filtered. To the filtrate, excess of acetic acid was added, and in some hours uric acid crystals of various forms, and giving the murexide test, were formed. In *Helix*, the acid occurs in combination with soda. W. D. H.

Absolute Acidity of Animal Fluids: Neutralisation of Orthophosphoric Acid. By C. Blarez (*Compt. rend.*, **103**, 264—267).—A decinormal solution of orthophosphoric acid was mixed with an excess of lime-water of known strength, and the mixture was either filtered at once or allowed to stand for a definite time and then filtered, care being taken to avoid contact with carbonic anhydride. The filtrate was titrated, and the lime left uncombined was thus estimated. It was found that by prolonged treatment with water, the precipitates gave up a certain amount of lime, and this also was estimated. From the results of his experiments, the author concludes that in presence of excess of lime, phosphoric acid forms compounds which contain a higher proportion of calcium than the normal salt. When 5 mols. of calcium oxide are brought in contact with 2 mols. of phosphoric acid (H_3PO_4), the compound $P_2O_5,3{\cdot}6CaO$ is formed; but if this is washed repeatedly with water, it has the composition $P_2O_5,3{\cdot}3CaO$. Similar compounds are obtained if phosphoric acid is supersaturated with sodium or potassium hydroxide, and mixed with calcium chloride. Analogous results are obtained with barium and strontium, and it follows that the basicity of orthophosphoric acid cannot be accurately determined since it varies with the conditions. Many animal fluids contain phosphates and phosphoric acid, and it follows that their acidity cannot be determined absolutely, but will vary with the conditions. C. H. B.

Snake Poison. By R. N. Wolfenden (*J. Physiol.*, **7**, 327—370).—With regard to the venom of the Indian cobra (*Naja tripudians*), it is found that its toxicity is not due to any bacterium or living organism, nor to any alkaloïd—alkaloïds and ptomaïnes are entirely absent from the venom—nor is it due to any cobric acid such as was described by Blyth (*Analyst*, **1**, 204). The author finds that the crystals to which the name cobric acid was given are in reality composed of calcium sulphate. The venom, however, is sometimes faintly acid, sometimes neutral. The poisonous properties of the venom are due to its proteïd constituents, which are as follows:—(1) Globulin, which is always present and kills by causing asphyxia. (2) Syntonin, which is precipitated with magnesium sulphate with the globulin. It dialyses through parchment paper to some extent. The poisonous property of the acid dialysates is due to this proteïd, not to cobric acid. Its action is similar to that of the globulin, but less intense. (3) Serum albumin; this is also toxic, producing

paralysis. (4) Traces in some specimens of hemialbumose, and questionable traces of peptone are regarded as accidental.

With regard to the venom of the Indian viper (*Daboia Russellii*), it is found to be of the same reaction as that of the cobra; but here again there is no toxic acid, alkaloïd, or living organism, but the proteïds are the poisonous constituents; these are three in number:—(1) Globulin, which greatly preponderates as in cobra venom; (2) Serum albumin in small amount; (3) A proteïd which possesses many of the properties of an albumose. True peptones do not occur, and it is probable that the substances described by Weir, Mitchell, and Reichart in crotalus, copperhead, and mocassin venoms as peptones are in reality albumoses. W. D. H.

Action of Tin on the Animal Organism. By T. P. White (*Pharm. J. Trans.* [3], **17**, 166—168).—Stannotriethyl acetate and sodium stannous tartrate were employed, and some 150 experiments were made with frogs, rabbits, and dogs. Frogs receiving 1·5 mgrm. of stannotriethyl acetate were completely paralysed the following day, whilst doses of 2·5 to 5 mgrms. caused death in 8 to 10 hours. With the sodium stannous tartrate, 15 to 20 mgrms. injected under the skin killed frogs in four or five days, and when 5 mgrms. was administered every four days, death ensued in three or four weeks. In all cases the central nervous system is affected, producing paralysis accompanied by diminution of the power of the heart. Rabbits immediately after an intravenous injection of 5 mgrms. are seized with transitory heaviness, followed in an hour or two by diarrhœa, colic, and ultimately death. Dogs injected with 25 mgrms. in vena saphena, howl, pass water and fæces, and in a few minutes intermission of respiration and failing of the heart's action ensue; by the use of artificial respiration, the animal recovers, but in an hour or so is attacked in a manner similar to the second set of effects with the rabbits. Post-mortem examinations show:—Heart in diastole, blood thin and dark; lungs collapsed and hyperæmic; intestines and stomach soft and very hyperæmic; mucus membrane easily loosened, covered with mucous, and slightly inflamed; liver pale, but somewhat enlarged; urine in bladder contains albumin. Experiments with the double salt confirmed these results, but much larger quantities had to be employed. When stannotriethyl acetate was administered per orem in small doses daily, or in larger doses at longer intervals, the animals died of the above symptoms after 10 or 14 days. Sodium stannous tartrate was not so effective, 240 to 360 mgrms. given to rabbits at long intervals caused death usually in the third week. With dogs, however, receiving even more than 60 mgrms. daily, only the hind legs and digestion are weakened for the time. In fact, the tin is not absorbed into the system, but passes away in the urine and fæces; when opium and bismuth are given along with it the effect is more pronounced. The blood and urine of a rabbit 48 hours after injection of 5 mgrms. of stannotriethyl acetate contained no tin, whereas with the double salt traces of this metal were found in the blood four to five days after injection, and in the urine after 12 hours. The stannotriethyl acetate is evidently readily decomposed in the blood, whilst the double salt is not; this

explains the activity of the former and the sluggishness of the latter of these two substances when introduced into the animal organism. Examination of the parts of a rabbit after being visibly affected by injection with 30 mgrms. of tin, showed that the muscles contained 0·0078 per cent. of tin; the heart, liver, and kidneys 0·0083 per cent.; the brains 0·025 per cent. In a dog receiving 150 mgrms. tin as double salt, after five days 340 grams of blood contained no tin, 235 grams of liver contained 0·0024 gram, 41 grams of brain 0·001 gram. The action of tin on and in the digestive tract and on the nervous system is explained. From other experiments, the author concludes that tin is entirely devoid of danger when taken internally in any form that could arise from being in contact with fruits or vegetables, and such cases of accidental poisoning attributed to tin he believes were due to solder or impurities—arsenic, copper, and lead.

D. A. L.

Chemistry of Vegetable Physiology and Agriculture.

Ferments. By A. Hansen (*Ann. Agronom.*, 339—340; from *Bot. Zeit.*, 1886, 137).—The author has examined the latex of different species of plants for the presence of ferments. He finds none in the Euphorbiaceæ, in *Ficus elastica*, *Scorzonera*, *Taraxacum*, or the juice of the opium poppy. The latex of *Ficus Caricà*, on the other hand, contains principles capable of effecting four fermentative changes; they peptonise albuminoïds in the presence of either alkalis or acids, act like diastase on starch, and coagulate the caseïn of milk. 20—100 grams of fibrin previously caused to swell by immersion in hydrochloric acid of 0·2 per cent. strength, are completely dissolved in 10—30 minutes when treated at 40° with 2—3 c.c. of this latex. The products of this digestion are the same as with pepsin, yet the two ferments are not identical, since the ficus latex peptonises in presence of alkalis as well as acids, although more slowly. Probably there are two peptic ferments present, one acting in acid, the other in alkaline solutions. By digestion with hydrochloric acid, the latex entirely loses its peptonising properties; digested with sodium carbonate (which destroys the activity of pepsin) it retains them intact. If a few drops of the latex be added to milk, which is then raised to the boiling temperature, the caseïn is at once precipitated. Incipient ebullition therefore does not destroy the curdling power of this latex, although prolonged ebullition does, and even a temperature of 65° if continued for two hours. The diastatic action of this latex is demonstrated by the partial transformation of starch-paste and glycogen into sugar. When the latex is precipitated by alcohol and the precipitate taken up with water, the action on milk and on starch is found to persist, whilst that on fibrin disappears.

The latex of *Carica papaya* peptonises, precipitates caseïn, and transforms starch into sugar.

The author does not consider that these vegetable ferments play any *rôle* in the nutrition of the plant (compare Martin, this vol., p. 641 and 642, and Green, *ibid.*, p. 826). J. M. H. M.

Activity of Fungoid Ferments. By N. W. Diakonow (*Bied. Centr.*, 1886, 575—576).—This is a preliminary report of the author's observations, which lead him to the following conclusions, namely, that the production of carbonic anhydride, in the absence of free oxygen, is not an invariable property of the living cell, but is dependent on the nutritive matter in which it exists; the presence of glucose is indispensable; the production of carbonic anhydride ceases when the oxygen of a solution is exhausted, and when the glucose is exhausted. The dissociation of the molecule of albumin does not produce carbonic anhydride in the absence of free oxygen, glucose being the only material which furnishes sufficient oxygen for that purpose. The organisms live for a time, but quickly die in the absence of oxygen, and there is a marked contrast between them and others supplied with a sufficient supply of it. The intensity of the production of carbonic anhydride by microscopic fungi diminishes with the increasing acidity of the solution when oxygen is absent, although under normal conditions the existence of the fungi is not affected by this cause. J. F.

Microscopic Fresh Water Algæ. By E. Bréal (*Ann. Agronom.*, **12**, 317—332).—When seeds are allowed to germinate in contact with fresh water, they yield a little organic matter to the water. If the water be then exposed to light, it soon becomes green throughout from the multiplication of minute green algæ, and is found to contain beside colourless organisms, infusoria, bacteria, &c. The green unicellular algæ, which have been made the subject of a number of observations by the author, are minute oval or spherical bodies seldom exceeding $\frac{5}{1000}$ of a millimetre in diameter. They are single, or in groups of two or three, with an integument derived from the mother cell, and multiply by means of zoospores. They contain chlorophyll, and are in fact simply microscopic plants, but being very widely diffused and abundant in nature they fulfil important functions. Under the action of light, they actively decompose carbonic anhydride dissolved in the water, and this soon becomes saturated with oxygen, the excess of which either goes to support infusorial life or escapes into the air. They also decompose bicarbonate of lime dissolved in the water, and thus give rise to a calcareous deposit. Being able to live in neutral or slightly alkaline liquids, they may, by the oxygen which they disengage, serve to oppose or even arrest putrefaction. Light is absolutely essential to their development and to their reproduction by zoospores. They rapidly remove nitrates and ammonia from water, since these two substances supply the nitrogen necessary to their growth; in the dark, however, liquids charged with these algæ evolve ammonia. J. M. H. M.

What is Diastase? By J. FRANKHAUSER (*Ann. Agronom.*, **12**, 340—341; from *Der Bund* (*Berne*), **37**, 126).—The author has studied both chemically and microscopically the transformation of starch into sugar and the solution of the cellular membranes which occur during the germination of barley. A grain of barley moistened with water, swells, and absorbs a perfectly definite quantity of the latter, and it appears to be the embryo which first absorbs the liquid. Respiration then commences and the temperature rises to 30°. During the development of the embryo, the albumin undergoes great modification, the cell walls become softened, and are in great part dissolved by the time the embryo has grown to two-thirds or three-fourths the length of the grain. Up to this time, the layer of gluten cells retains the cell wall, and the starch of the grain is still intact. Are the softening and solution of the cell walls effected by diastase secreted by the embryo, or by the intervention of microbes as held by Duclaux and Pasteur? The author has failed to detect microbes after the most careful search, and therefore attributes the action to diastase, or at any rate to some analogous chemical agent, since diastase itself is still an unknown substance. Besides carbonic acid, certain stronger acids are generated, during the germination of potatoes and barley for example, and Frankhauser has succeeded in separating formic acid by operating on large quantities of malt by treatment with 5 per cent. potash and distillation. He finds that this formic acid, as well as the commercial article prepared from other sources, possesses the property of transforming starch into sugar. The author supposes that the formic acid secreted by the embryo attacks first the cell walls nearest it, being readily absorbed and conducted by them; after the embryo has been killed by drying, the formic acid attacks the starch in exactly the same way as sulphuric acid would do.

J. M. H. M.

Assimilation of Asparagin by Plants. By P. BAESSLER (*Landw. Versuchs-Stat.*, 1884, 231—240).—Maize plants placed in a solution containing asparagine, will not grow for long, their roots become diseased, &c. It was arranged that the plants should be in a solution containing the usual mineral constituents only for a few hours, and then be transferred to a solution of asparagine; this answered fairly well, and a full description is given of the appearance of the plants thus grown when compared with others which did not receive asparagine, as also descriptions of the plants when grown under other conditions; those grown in asparagine contained much less dry matter but more nitrogen than those under normal conditions. Some plants were also supplied with potassium nitrate in place of asparagine, but both sets having been in the nitrogenous solution were transferred to a normal nitrogen-free solution for some time, and then back to the asparagine and nitrate solutions respectively; as regards the development of the plant, the nitrate solution was rather the most effective, and the percentage of nitrogen present in the plant was slightly higher, yet the experiments show that asparagine can be assimilated by plants with as good results as nitrate if decomposition products of the amide are avoided, and this was done in the present

case by permitting the plant to remain in the solution of asparagine for a short period of time only. E. W. P.

Absorption of Carbonic Anhydride by Leaves. By Dehérain and Maquenne (*Compt. rend.*, **103**, 167—169).—10 grams of fresh leaves were brought into contact with a known volume of carbonic anhydride at a constant temperature. The proportion of carbonic anhydride absorbed by leaves under atmospheric pressure increases with the proportion of water contained in the leaves, but diminishes with a rise of temperature. The coefficient of absorption of carbonic anhydride by the water in the leaves, within ordinary limits of temperature, is greater than the coefficient of solubility of the gas in pure water. At ordinary temperatures, the absorption is instantaneous, but at 0° it is slower, and requires five or six minutes.

C. H. B.

Composition of Vines. By A. Hilger and L. Gross (*Landw. Versuchs-Stat.*, 1886, 170—196).—A large portion of this article is occupied by a *résumé* of the work of others on the same subject, and with the analytical details, which are given in full. All parts of the vine, the leaves, fruit, stalks, &c., at all ages were examined as regards organic constituents and ash. In the exuded sap from the cut vines were found saccharose, calcium tartrates, citrates, and succinic acid, inosite, and an unknown mucilaginous extractive; in the young shoots and leaves, "tartar," calcium tartrate, quercetin, quercetrin, tannin, starch, tartaric and malic acids, gum, inosite, glucose, saccharose, oxalic and glycollic acids, also a substance extractable by ether, ammonium compounds, calcium phosphate and sulphate; in autumn inosite and malic acids are absent from these parts of the plant. In the tendrils, the author found sugar, "tartar," calcium oxalate, and a not inconsiderable quantity of some pectous substance; in the fruit were found tannin, tartaric and malic acids, as well as their calcium and potassium salts, succinic, glyoxylic, and glycolic acids, inosite, dextrose, and levulose, albuminates, colouring matters, and traces of quercetin and quercitrin. The ashes of the fruit with their stems and that of the tendrils are rich in phosphates and alkalis, whilst the ashes of the leaves and wood are remarkable for the large quantity of lime and carbonates present; magnesia is evenly distributed, ranging from 1·5 per cent. in the tendrils to 1 per cent. in the ripe fruit. Iron and silica are found principally in the leaves, and only as traces in the tendrils. The percentage of sulphates is very variable.

E. W. P.

The Presence of Mannitol in the Cambium Sap of Pines. By J. Kacher (*Monatsh. Chem.*, **7**, 410—415).—On evaporating the sap from the cambium layer of pines, to about one-fifth of its original bulk, acicular crystals of mannitol separate gradually. There are also present coniferin and a compound containing manganous oxide, magnesia, and oxalic acid; this is deposited as a sandy powder from the mother-liquors of the mannitol with dextrose, formed by some fermentation process. V. H. V.

Development of the Sugar-beet. By A. Girard (*Compt. rend.*, **103**, 159—162).—Mainly a summary of papers which have already appeared. In the early stages of its growth, the energies of the plant are chiefly directed to the formation of leaves and rootlets, but after the middle of the second month, the growth of the root becomes proportionally very rapid, and the sugar formed in the leaves is stored up in it, together with water and inorganic salts taken up from the soil by the rootlets. C. H. B.

Accumulation of Sugar in the Root of the Sugar-beet. By L. Brasse (*Ann. Agronom.*, **12**, 305—317).—The accumulation of reserves of insoluble materials, in various parts of the vegetable organism, has found its complete explanation at the hands of Dehérain. That author, by an application of the known laws of diffusion, shows that if a dialysable substance is rendered insoluble or precipitated within certain cells of a plant as fast as it diffuses in from without, a reserve of it will be stored up within those cells, because more and more of the substance will find its way through in order to restore the equilibrium (as regards strength of solution within and without the cells) which is constantly being disturbed by the precipitation. The storing up of soluble reserves, as for example cane-sugar, in the beetroot, is not very susceptible of this explanation, since even if it be admitted that the cane-sugar forms an insoluble compound with protoplasm within the root-cells, the fact has to be accounted for that in the commercial process of extraction, the whole of this sugar is yielded to the water employed in the diffusion process.

The following is the author's explanation:—Cane-sugar forms a non-dialysable compound with protoplasm, which compound has a certain tension of dissociation; that is to say, if it is in contact with a sugar solution of less than a certain strength, a portion of the compound breaks up, and sugar passes into solution until the critical strength is reached; if brought into contact with a stronger sugar solution than this, a portion of the sugar in the solution combines with protoplasm, should there be an excess of the latter, until the critical strength is again reached. In support of this explanation, the author cites several series of experiments on beetroots of different degrees of richness in sugar. The sugar being carefully determined in slices in these roots, duplicate slices were placed for 24 or 48 hours in sugar solutions of different strengths, kept at 10°, and any increase or diminution in the strength of these solutions was then determined in a pipetted portion. It was always found that the weaker solutions of sugar increased in strength by contact with the beetroot, whereas the stronger solutions diminished in strength. For example, a slice of a very rich root, containing 24·8 per cent. of sugar, placed in a solution containing 2·4 per cent. of sugar, increased the strength of the latter in 24 hours to 2·6 per cent.; placed in a 5 per cent. solution of sugar it effected a reduction to 4·9 per cent.; and a 10 per cent. sugar solution marked after the immersion only 9·8 per cent. It should be noted that the beetroot withdrew sugar from the last two solutions, although they were much poorer in sugar than the juice of the beet itself. A precisely similar slice of this

root was chloroformed and placed in solutions of the strengths already mentioned. In this case, all the solutions were strengthened by contact with the beetroot, so that the property of withdrawing sugar from solutions weaker than its own juice, but above a certain critical strength, appears to belong to the root only while all its contents are in a living or active condition. In another set of experiments, the author proves that the living beetroot does not withdraw sugar from the solutions by mere imbibition of liquid, for he shows that a slice of root containing 11·36 per cent. sugar, when placed in a solution of 4·85 per cent., actually lost in water and gained in sugar at the same time. J. M. H. M.

Lecithin in Plants. By E. Heckel and F. Schlagdenhauffen (*Compt. rend.*, **103**, 388—390).—The plants were exhausted with light petroleum and chloroform, the liquid distilled off, the residue treated with potassium nitrate, the product dissolved in dilute nitric acid, evaporated to dryness and heated, and the aqueous solution of this residue was tested for phosphoric acid by means of uranium solution and ammonium molydate. Precipitates were obtained with the extracts from the juices of jequirity (0·050 per cent. P_2O_5), arachides (0·005 per cent.), fedegosa (0·235), fenugreek (0·266), black mustard (0·040), and white mustard (0·035), and from the fatty substances from the leaves of *Erythroxylon hypericifolium* (0·010), the roots of *Phrynium beaumetza* (0·100), and the leaves of *Globularia alypum* (0·005). No precipitates were obtained from the following oils:—Olive, sesame, linseed, cotton-seed, poppy, laurel, and castor-oil.

The phosphorus can only have been derived from lecithins, and this conclusion is confirmed by the fact that when some of the oils which yield most phosphoric acid are saponified by baryta, the soaps contain both glycerol and phosphoric acid. C. H. B.

Chemical Examination of the Fruit of Daphnidium Cubeba. By J. O. Braithwaite and E. H. Farr (*Pharm. J. Trans.* [3], **17**, 231—233).—The fruit of *D. cubeba* bears some resemblance to genuine cubebs (*Piper cubeba*); therefore, investigations were made to determine the points of distinction. The botanical character and distinctive features are noted, and all methods and processes of separation in the chemical examination are fully described. The dry pulverised drug was successively exhausted with light petroleum, ether, alcohol and water. The petroleum extract (24·2 per cent.) contained 1·25 per cent. volatile oil of a pale-yellow colour, solid at 155°, melting point 17°, sp. gr. 0·911, soluble in alcohol and chloroform in all proportions, insoluble in carbon bisulphide; it is noteworthy that this volatile oil gives yellows or browns with reagents which produced violets or blues with the volatile oil of cubebs. The non-volatile portion consists chiefly of lauric, capric, and oleic acids, and some resin. The ethereal extract (11·5 per cent.) contained two alkaloïds, three resins, and a trace of a glucoside-resin. One alkaloïd, not precipitated by lead acetate, forms a crystalline hydrochloride, acetate, platinochloride and aurochloride, gives precipitates with alkaloïd reagents, but produces only negative colour reactions; the

other alkaloïd is precipitated by lead acetate and yields crystalline salts, but gives neither the usual precipitates nor colours. Of the resins one is insoluble in benzene; the other two are soluble in this medium, but only one of them dissolves in carbon bisulphide. The alcoholic extract (3·5 per cent.) contained two neutral resins, a glucoside resin, and a trace of alkaloïd. The water extract (5·8 per cent.) contained neither alkaloïd, glucoside, nor sugar. The ether residue has an aromatic bitter taste, and less than 0·1 gram caused purging and vomiting. The fruit contained 5·34 per cent. moisture and 5·998 per cent. ash. D. A. L.

Examination of the Leaves of Æsculus Hippocastanum and of Acer Dasycarpum. By F. O. Ray (*Pharm. J. Trans.* [3], **17**, 108).—The leaves of the horse chestnut (*E. hippocastanum*) and of silver maple (*A. dasycarpum*) have been examined and found to contain neither cocaïne, caffeïne, nor other principles of special interest. Even æsculin is absent from the leaves of horse chestnut.
D. A. L.

Proteïds of Wheat Flour. By S. H. C. Martin (*Brit. Med. J.*, 1886, **2**, 104—105).—Gluten does not exist in flour as such, but is formed by the action of water (perhaps also by a ferment action) on the proteïds pre-existent in the flour. The doctrine of a ferment action is supported by the fact that washing flour with water at a low temperature (2°) does not lead to the formation of gluten. Gluten is insoluble in cold water, and in 10 to 15 per cent. sodium chloride solution. It dissolves partially in alcohol and in boiling water. Both these extracts contain the same substance, which is an albumose, and to which the name "*insoluble phytalbumose*" is given; it corresponds with two substances, called by Ritthausen gliadin and mucedin. It gives the stickiness to gluten. The insoluble residue is called *gluten-fibrin*. Boiling water, besides dissolving out the insoluble albumose, coagulates the residue, gluten-fibrin. Gluten-fibrin can be completely dissolved by 0·2 per cent. hydrochloric acid: both it and insoluble phytalbumose are converted into true peptones by means of pepsin and trypsin. Flour itself contains two proteïds: (1) Globulin of the myosin type coagulating between 55° and 60°, precipitated by sodium chloride and magnesium sulphate; (2) soluble albumose. Both these proteïds can be extracted from flour by means of a 10 to 15 per cent. sodium chloride solution. They are considered to be the precursors of gluten, according to the following scheme:—

$$\text{Gluten} = \begin{cases} \text{Gluten-fibrin—precursor, globulin} \\ \text{Insoluble albumose—precursor, soluble albumose.} \end{cases}$$

W. D. H.

Composition of Barley Fat. By A. Stellwag (*Bied. Centr.*, **15**, 573).—The fat obtained from ground barley by extraction with ether, when placed in a vacuum drying oven at 40—45°, becomes a yellow-brown oil; when left for a time, a firm, crystalline fat separates, leaving about half the original oil fluid at ordinary temperatures; the solid fat melts at 13°, and 1 gram requires 182·7 mgrms. of alkali for saponification, in this resembling the fats of other

cereals. All seeds of the cereals contain a large proportion of free fatty acids; that of the barley under examination yielded 13·62 per cent. of free fatty acids and 77·78 per cent. of neutral fat, besides a fat containing phosphorus, and which calculated to lecithin, amounted to 4·24 per cent.; besides the saponifiable fats, plant fats contain other substances, such as cholesterin. The composition of barley fat is as follows:—

Free fatty acids	13·62 per cent.
Neutral fats	77·78 „
Lecithin	4·24 „
Cholesterin	6·08 „

The examination of malt combings shows that the fat is probably transformed into cholesterin and similar wax-like bodies during germination. J. F.

Waste Water from Starch Factories. By R. Schütze (*Landw. Versuchs-Stat.*, 1886, 197—201).—The waste water from starch factories contains acetic, propionic, butyric, and lactic acids, as well as starch, albuminoïds, &c. These compounds, under certain circumstances, form a good nidus for the production of the lower organisms; consequently, from a hygienic point of view, it is of importance to get rid of this liquid, of which analyses are given. It is proposed to heat the liquid in properly arranged vessels to a temperature of 60—70°, and to add thick milk of lime until alkaline reaction sets in, and then add more liquid to render the mass slightly acid. The yellowish-brown precipitate having settled, may be dried, when it will be found to contain quantities of calcium phosphate, &c., varying according to the composition of the waste ("sour") water; there have been found:—Calcium phosphate, 26·6—35·09 per cent., crude proteïn, 8·69—33·85, and organic matter, 5·87—38·08. Such a compound is said to be well adapted as food for pigs, when given in combination with brewer's grains. E. W. P.

Oxygen in the Air of Forests. By E. Ebermeyer (*Bied. Centr.*, **15**, 505—506).—The method of determination was that of Lindeman, namely, absorption by dilute phosphorous acid, the only instruments required being a Hempel gas pipette and measuring tube. Determinations were made in 20 localities in Bavaria, the season being late in summer and early in autumn; the average of oxygen in forest air and that of the open country was respectively 20·78 and 20·82 per cent. by volume. The difference is unimportant, but the freedom from dust, smoke, and micro-organisms renders the air of the country far preferable to that of towns. The author enumerates many other well-known reasons for preferring residence in a wooded country. J. F.

Dried Beer Grains as Horse Fodder. By Sattig (*Bied. Centr.*, 1886, 539—540).—The high price of oats, the cheapness of potatoes, and the introduction into commerce of dried beer grains induced the author to compound five mixtures of these substances, on which he

fed 22 horses ranging from 6 to 19 years old. They were engaged fully on the usual work of the farm; the results were quite satisfactory, the young horses increasing well in weight and all keeping in good condition. The following is the composition of the various rations in kilograms; the potatoes were given uncooked:—

No. 1.	Hay, 2·5;	potatoes, 12·5;	grains, 2·0;	oats, 0·5.	
„ 2.	„ 2·5;	„ 12·5;	sesame cake, 0·75;	wheat chaff, 2·0.	
„ 3.	„ 2·5;	„ 12·5;	grains, 2·5.		
„ 4.	„ 2·5;	„ 12·5;	„ 2·0;	linseed cake, 0·5.	
„ 5.	„ 5·0;	oats, 5·0.			J. F.

Composition of Certain Cattle Foods. By Dietrich (*Bied. Centr.*, 1886, 57).—The following analyses were made at the experimental station of Cassel: the cakes were tested for fat and proteïn only; the other substances were fully examined; the number of cake samples was large:—

	Fat.			Proteïn.		
	Average.	Min.	Max.	Average.	Min.	Max.
Cotton-seed cake..	14·3	9·8	17·6	43·3	39·8	48·7
Do. ..	13·55	9·3	18·3	43·8	40·1	45·6
Sesame cake.....	14·1	9·4	17·7	37·4	34·6	41·1
Rape cake.....	9·6	7·4	11·4	33·6	30·3	36·8
Poppy-seed cake..	10·3	6·2	15·0	37·3	35·6	39·8
Rice-flour cake....	?	2·8	18·9	?	5·7	17·8

The following is a selection from a longer list:—

	Water.	Proteïn.	Fat.	Nitrogen-free extract.	Cellulose.	Ash.
Clover hay.....	15·0	13·98	3·57	36·06	23·93	7·46
Wheat chaff	15·33	3·81	1·62	44·39	22·91	11·94
Oat straw	15·0	7·58	2·66	28·62	28·32	7·62
Meadow hay	15·0	13·11	1·76	39·13	17·55	13·45
Do. well saved	14·45	11·93	3·51	44·76	17·76	7·59
Second crop hay ..	15·18	12·87	3·94	42·06	16·78	9·17
Barley straw.....	13·11	5·25	1·77	36·62	38·67	4·58
Dried malt grains..	16·95	17·87	6·59	41·69	13·84	3·06

J. F.

Jensen's Manner of Protecting Potatoes from Disease. By F. Nobbe (*Bied. Centr.*, 1886, 549—553).—The author reports experiments made with the system recommended by Jensen, which consists of earthing the stalks highly (see Abstr., 1885, 1154. A special plough has been constructed for the purpose). The experimental fields were free from the disease, although from the author's remarks it seems it prevailed in the district.

The experiments were continued for three years, and in all cases the tubers continued free from the disease; in some cases scab was found, but not to a great extent.

It was found that the total yield of crops so protected was less than

control plots not treated; in 1883, the loss was 23·03 per cent.; in 1884, 10·24 per cent.; in 1885, 15·42 per cent. This loss is accounted for by the injury done to the leaves and stalks during the process; the author nevertheless recommends the system to farmers, to be tested, at least, in an experimental way. J. F.

Manuring of Turnips. By C. Brown (*Ann. Agronom.*, **12**, 346—349, from *Agricultural Gazette*, March 8, 1886).—The experiments of 1885, which were similar to those carried out by the author for a number of years before, were intended to throw light on the following points:—

a. To what extent a turnip crop, grown on a typical Norfolk soil, may be benefited by the application of potash manures. *b*. What increase would result from the addition of available nitrogen to the turnip manure, and the best form in which to apply it. *c*. The comparative value of dissolved and undissolved phosphates. *d*. The value, if any, of magnesia salts.

Long plots, of half an acre each, were drilled with turnips and dressed respectively with dissolved bones, "turnip manure," superphosphate, superphosphate and greaves, superphosphate and ammonium sulphate, superphosphate and sodium nitrate. The plots were then divided transversely into four equal parts, three of which were cross-dressed with potassium chloride, magnesium sulphate, and kainite respectively, the fourth receiving no additional dressing. Besides these, there were two plots that received no manure, and two plots dressed with $\frac{1}{2}$ cwt. ground coprolites only.

The yields obtained in these experiments varied from 9 tons 12 cwts. and 10 tons 1 cwt. per acre on the two unmanured plots, to 21 tons 18 cwt. on the plot receiving turnip manure and kainite, and 21 tons 1 cwt. on the plot receiving superphosphate, sodium nitrate, and potassium chloride. The "compound turnip manure" consisted of one part ammonium sulphate, one part potassium chloride, and three parts superphosphate. The average Norfolk soil, on which these turnips were grown, was about 18 inches deep, resting on chalk; it contained by analysis 0·23 per cent. of potash soluble in hydrochloric acid. The addition of the potash salt or kainite to the other manures was in every case followed by an increased yield; for example, whereas superphosphate + sodium nitrate gave 15 tons 15 cwt., and superphosphate + ammonium sulphate 16 tons 3 cwt., the same manures with the addition of 2 cwt. per acre potassium chloride gave 21 tons 1 cwt. and 20 tons 14 cwt. respectively. Magnesia salts produced little, if any, beneficial effect. 1 cwt. potassium chloride produced on the average about the same increase as 4 cwt. kainite. The plots receiving ground coprolites gave exceedingly poor yields, namely, 10 tons 17 cwts. and 10 tons 1 cwt. Contrary to expectation, superphosphate and greaves gave no better crop than superphosphate alone. Ammonium sulphate and nitrate were equally efficacious as additions to superphosphate; the superphosphate alone gave an increase of about $4\frac{1}{4}$ tons per acre over the unmanured plots; with sodium nitrate or ammonium sulphate, this increase was raised to $6\frac{3}{4}$ tons. 5 cwt. per acre of dissolved bones, containing 2·74 per cent.

ammonia, 19·73 per cwt. soluble sulphate, and 11·67 per cent. insoluble and precipitated phosphates, gave about the same increase as 4 cwt. superphosphates and $1\frac{1}{2}$ cwt. sodium nitrate.

The plots receiving potash salts were observed to suffer much less from drought than the others. J. M. H. M.

Manurial Experiments with Precipitated Phosphates and Thomas Slag. By H. Schönemark and others (*Bied. Centr.*, 1886, 524—534).—These experiments on the relative manurial value of the phosphatic materials were carried out at the experimental station of Cunrau, where moorlands in various stages of reclamation are under control.

The general rule was that each plot should receive the quantity of potash required for development of the plant in the form of kainite, but that the phosphoric acid should be applied in quantities of 25—40—55 pounds (German) per morgen, some in form of precipitated calcium phosphate, others as ground Thomas slag; the plants selected were oats, barley, and potatoes.

With oats, the slag produced somewhat less grain and much more straw than the precipitated calcium phosphate, but as the results of the whole series of experiments, the author is of opinion that the manurial value of the phosphoric acid in both manures is equal, the slag, however, is much the cheaper.

It was also found that under the conditions of the trials, the use of more than 25 pounds of phosphoric acid per morgen did not produce a commensurate increase of crop.

The latter portion of the article traces the effects of continued cultivation on moorlands, the accumulation of fertilising ingredients, their increased solubility and assimilability. J. F.

Action of Various Forms of Phosphoric Acid. By J. Fittbogen (*Bied. Centr.*, 1886, 520—523).—These experiments were made in continuation of those previously noticed (Abstr., 1885, 1009); they were carried out with young barley plants, grown in sterilised sand contained in glass pots, to which was added, in all cases, a mixture of nutritive salts, calcium chloride, magnesium sulphide, calcium nitrate, &c. The phosphates selected were monocalcium phosphate, dicalcium phosphate, and Thomas slag, both in the raw state and prepared according to certain patented processes; in one of each series of experiments humic acid, and in another calcium humate was added.

The following conclusions have been arrived at by the author:—

Ground Thomas slag and its precipitates provide sufficient phosphoric acid for the production of a normal crop of barley.

The addition of humic acid to the ground slag has a rapid and vigorous effect, increasing the yield considerably.

Field experiments with oats and potatoes confirm the previous conclusions, Thomas slag being found as efficacious as the more costly manure. The author recommends the application of the slag as long as possible before sowing the seeds, and says that salts of ammonia should not be mixed with it, but applied after a considerable interval of time, as the caustic lime expels the ammonia. J. F.

Analytical Chemistry.

Chromatometer. By L. Andrieu (*Compt. rend.*, **103**, 281—284).—The quality of the colour is determined by comparing it with a ray of polarised light which gives the same colour, and the quantity of colour is measured by the thickness of the layer of solution at the moment when the comparison is made, the apparatus being so arranged that the thickness of this layer can be accurately adjusted; great care must be taken to secure identical conditions of illumination in order to make the indications of the same instrument comparable with one another. A description of the instrument would not be intelligible without the accompanying drawing.

C. H. B.

Washing and Drying Precipitates without Exposure to the Carbonic Anhydride of the Atmosphere. By A. Jolles (*Zeit. anal. Chem.*, **25**, 369—371).—A cylindrical glass vessel, having its edge well greased, is covered by a ground glass plate, through which there are three holes. Through the first, which is fitted with a stopcock-funnel, water is introduced; through the second, air purified by potash enters; the third is furnished with a glass stopcock syphon, which slides in the caoutchouc stopper, so that it can be lowered to the desired level after the precipitate has subsided. When the washing is complete, a porous clay cylinder is attached to the inner end of the syphon, and the outer limb is connected with a vessel from which the air is exhausted. The precipitate collects in a lump on the clay cylinder, from which it can readily be transferred to the desiccator.

M. J. S.

Normal Solutions and the Retention of Mohr's System. By B. Tollens (*Zeit. anal. Chem.*, **25**, 363—365).—The author deprecates the change proposed by Winkler (this vol., p. 96), on the ground of the confusion that would be introduced into chemical literature if the term "normal" were once to be applied to solutions of any other strength than that now universally recognised. He proposes the following formal definition:—"Normal solutions contain in one litre that quantity in grams of the active substance which in the reaction under consideration is equivalent to 1 molecule or 36·5 grams of hydrochloric acid."

M. J. S.

Apparatus for Determining Melting Points. By C. F. Roth (*Ber.*, **19**, 1970—1973).—The apparatus consists of a flask 65 mm. in diameter, with a neck 200 mm. long and 28 mm. wide. A tube 15 mm. wide closed at the lower end is fused into the opening of the flask; it is of such a length that it reaches within 17 mm. of the bottom of the flask. The neck of the flask is provided at its upper end with an opening which can be closed with a glass tap. Sulphuric acid is poured in through this until it reaches about half way up the neck of the flask. When heated, the temperature is nearly the same

in each part of the apparatus. A list of melting points determined with the apparatus is given to show that it gives good results. It cannot, however, be heated above 250°. N. H. M.

On the Use of Hydrogen occluded by Palladium as an Analytical Reagent. By SCHWARZENBACH and L. KRITSCHEWSKY (*Zeit. anal. Chem.*, **25**, 374—375).—Palladium hydrogen precipitates from their solutions silver, mercury (from the nitrates), gold, platinum, palladium, and copper in the metallic state; reduces acidified permanganates to manganous salts, ferric to ferrous salts, chromic acid to chromic oxide, potassium chlorate to hypochlorite, acetic acid to aldehyde and alcohol, and nitrobenzene to aniline. Salts of lead, bismuth, cadmium, arsenic, antimony, tungsten, molybdenum, zinc, cobalt, nickel, aluminium, cerium, uranium, rubidium, and cæsium, the alkalis and alkaline earths are not reduced. By employing the charged palladium in ample excess, and not leaving it too long in the solution, the reduction takes place with quantitative exactness.
M. J. S.

Note.—Gladstone and Tribe found that chlorate is reduced to chloride without the formation of any intermediate oxy-compound (Trans., 1878, 308).—M. J. S.

Substitution of Sodium Thiosulphate for Hydrogen Sulphide in Qualitative Analysis. By G. VORTMANN (*Monatsh. Chem.*, **7**, 418—428).—It is here proposed to substitute sodium thiosulphate for hydrogen sulphide for the precipitation of certain metals in qualitative analysis, as a less offensive and equally practicable reagent. In outline the method consists, after precipitation of the hydrochloric acid group of metals, and subsequent precipitation of lead, barium, strontium, and calcium in part as sulphates, in boiling the filtered solution with sodium thiosulphate solution (1 part of the crystalline salt in 5 parts of water); this precipitates copper, mercuric, bismuth, arsenic, antimony, and tin salts. The necessary conditions are: (i) That the solutions to be examined must not contain too much free acid, nor any nitric acid; (ii) the sodium thiosulphate must be added in small quantities at a time, and not in excess.

According to the author, the results are equally satisfactory with those obtained by the usual methods. V. H. V.

Determination of Nitrogen in Coal and Coke. By S. SCHMITZ (*Zeit. anal. Chem.*, **25**, 314—318).—The Dumas and Will-Varrentrapp methods give, especially with coke, low and discordant results. The following adaptation of Kjeldahl's process yields results which are higher and agree well amongst themselves:—About 1 gram of the coal, or 0·5—0·7 gram of coke, very finely powdered, is mixed with 1 gram of mercuric oxide and 20 c.c. of strong sulphuric acid, which is then heated for 2 to 3 hours to vigorous boiling. In the case of coke, a further quantity of 1 gram of mercuric oxide, and then 2 grams of powdered potassium permanganate, are slowly added after the first hour's heating. Frequent shaking is necessary. The cooled liquid is diluted, mixed with 140 c.c. of aqueous soda (1·25 sp. gr.), and then with a solution of yellow sodium sulphide

(1·4 gram of Na_2S for each gram of mercuric oxide). A fragment of zinc is added and the liquid is distilled (with precautions against spirting) into $\frac{1}{20}$ normal sulphuric acid, which is lastly titrated with $\frac{1}{20}$ normal baryta and rosolic acid.

Even this treatment fails to give correct results with coke which has been in the ovens for 48 hours or longer. M. J. S.

Estimation of Nitrogen in Milk and Urine of Herbivora. By H. Weiske (*Landw. Versuchs-Stat.*, 1886, 305—310).—The nitrogen in the urine of herbivora may be estimated with exactness either by Will-Varrentrapp's or by Kjeldahl's process, and the additional process of oxidation by permanganate may be employed according to desire, but with no advantage. The author finds that Kjeldahl's method yields higher, and therefore more correct results than Will-Varrentrapp's. This is opposed to the results obtained by Hornberger and others (*Landw. Versuchs-Stat.*, 1884, 254). E. W. P.

Sewage. By W. R. Nichols and C. R. Allen (*Chem. News*, **54**, 69—71).—Kjeldahl's method has been successfully applied to the determination of the total nitrogen in sewage. Fifteen samples of Boston sewage taken during May, 1885, were examined for ammonia, albuminoïd ammonia, total nitrogen, total solids, chlorine, and phosphoric acid, and showed considerable variation; for instance, the maximum and minimum of ammonia, total nitrogen, solids, and chlorine were in parts per 100,000: NH_3 11·94 max., 0·95 min.; N 17·15 and 1·81; solids, 640 and 178; chlorine, 311 and 59; and of P_2O_5, 7·035 and 0·096. Total solids and chlorine are high throughout, owing to the use of sea-water in factories and to the infiltration of sea-water. Fermentative tests indicate the presence of urea or some similar fermentable nitrogenous substance. D. A. L.

Azotometry and the Azotometer. By W. Knop (*Zeit. anal. Chem.*, **25**, 301—308).—The author has effected various improvements in the arrangement of his azotometer. A glass tube, with a stopcock at its upper end, and widened below into a stopper which is ground into the neck of the reaction flask, is filled with glass beads moistened with hypobromite. This absorbs and decomposes any traces of ammonia carried off by the gas. The reaction flask is sometimes made with an internal partition, dividing its lower part into two cells, in one of which is placed the hypobromite and in the other the nitrogenous substance. It is then easy to regulate the rate at which the nitrogen is evolved. The whole apparatus is immersed in water in a glass cylinder, with a tubulure through which passes the stopcock for adjusting the water level in the open limb of the U-tube. M. J. S.

Reduction of Ferric Nitrate in the Nitrometer. By T. Bayley (*Chem. News*, **54**, 52).—Ferric nitrate is shaken with sulphuric acid in the nitrometer, and after the appearance of the dark raspberry tint, the nitric oxide is expelled, and cold, recently boiled distilled water is added through the tap, avoiding entrance of air. When

cool, the liquid is allowed to flow into a freshly prepared solution of potassium ferricyanide, when the blue colour instantly appears. The following example is adduced as an instance of sulphuric acid containing sufficient iron to dissolve a measurable quantity of nitric oxide:—8 c.c. of a nitrous sample of Glover acid gave the dark raspberry tint and evolved 3·0 c.c. of nitric oxide, and on diluting with 8 c.c. of water, 0·5 c.c. of gas were liberated. The liquid had a chocolate colour, and in the author's opinion contained probably 1 c.c. of gas.

D. A. L.

Modification of Sonnenschein's Process for Determining Phosphorus in Iron and Steel. By N. Huss (*Zeit. anal. Chem.*, **25**, 319—326).—The author finds that before precipitating with molybdate, it is necessary to completely destroy the carbonaceous substances in the iron solution, since otherwise these reduce some of the molybdic acid to a lower oxide, which then separates together with the phosphomolybdate and is finally found in the magnesia precipitate, to which it gives a yellow colour. Simply roasting the residue from the evaporation of the nitric acid solution of the iron is not sufficient, but by subsequently dissolving it in hydrochloric acid and treating with potassium chlorate, the organic matters are entirely removed, so that the magnesium pyrophosphate is free from molybdenum. Results obtained in this way were about one-fourth lower than when roasting only was employed. Another means of avoiding the presence of molybdenum in the magnesia precipitate is to add an excess of bromine to the ammoniacal solution of the phosphomolydate precipitate, and after a few minutes to restore the alkalinity by adding ammonia.

If, however, the result is obtained by weighing the phosphomolybdate precipitate, the error caused by reduced molybdenum oxides may be neglected, owing to the very small percentage (1·63) of phosphorus. The following method, which is a very rapid one, has given good results:—10 grams of the steel is dissolved in 200 c.c. of nitric acid of 1·2 sp. gr. The solution is boiled for 15 minutes, then cooled and mixed with the exact quantity (28·65 grams) of ammonium chloride required to form ferric chloride; 50 c.c. of a 20 per cent. solution of ammonium molybdate is added, and the mixture is heated to 50°. Filtration can be commenced in 15 minutes. The precipitate is first washed with a solution of ammonium molybdate in dilute nitric acid, then with warm 1 per cent. nitric acid. It is dried at 80°, removed from the filter which is gently incinerated, and, after a few minutes further drying is ready for weighing. The omission to remove silica (when working on steel from the basic process) does not affect the result appreciably.

M. J. S.

Determination of Arsenic. By F. Reich and T. Richter (*Zeit. anal. Chem.*, **25**, 411—412).—Half a gram of the substance is warmed with strong nitric acid; the greater part of the acid is evaporated off; 4 grams of sodium carbonate and 4 grams of potassium nitrate are added, and the dried mass is fused for 10 minutes. After cooling, it is dissolved in water and feebly acidified with nitric acid. A solution containing 1 gram of silver is added, and then

dilute ammonia to neutrality. The precipitate is collected, washed, dried, fused with 10 assay-centners of test lead and some borax, and the silver determined in the usual way; 100 parts of silver correspond with 23·15 of arsenic. M. J. S.

Copper Reduction Test for the Estimation of Arsenic. By H. Carmichael (*Amer. J. Sci.*, **32**, 129—132).—Using a standard square of copper as an indicator, the author adopts the following method for the estimation of small quantities of arsenic. A clean, smooth, polished sheet of pure copper, 0·05 mm. thick, is cut into pieces 20 by 21 mm. A strip 1 mm. wide is cut nearly across the longer side, and bent at a right angle to the general surface; the bent strips forming the handles for manipulating the squares. The substance under examination is digested with strong sulphuric acid, the solution reduced to a small volume, and strong hydrochloric acid added. If the substance can only contain arsenic in the arsenious form, it is reduced to a small volume of liquid, and strongly acidified with hydrochloric acid. The acidified solution is brought into a porcelain capsule, and a square of copper introduced. The capsule is placed over a small flame; and the square moved to and fro until it acquires the tint of the standard chosen. The copper is then removed, washed, and dried. The strength of the acid is maintained, and squares made to succeed one another until there is no further discoloration. The total amount of arsenic present is obtained by multiplying the number of squares by the volume of standard arsenious solution necessary to colour equally a single square, and subtracting an amount which it is shown by trial the last square has required less than a normal square. The method is illustrated by details of the analysis of a sample of wall-paper and of a human stomach. A copper square 1 mm. side is capable of disclosing and estimating 0·0000025 gram of arsenious oxide. B. H. B.

Estimation of Caustic in Causticised Soda Liquor. By W. Upward (*Chem. News*, **54**, 67).—Precipitation with barium chloride and subsequent titration is resorted to; it is important to wash out the caustic alkali from the precipitate, and to work uniformly. For the estimation of carbonate, the precipitate is treated with excess of standard acid and titrated back with standard soda. D. A. L.

Displacement of Ammonia by Alkaline Bases. By Berthelot and André (*Compt. rend.*, **103**, 184—187, and 299—301).—A continuation of the discussion with Schloesing. The authors have made new experiments, and find that lime and magnesia are unable to expel the ammonia from double salts, such as ammonium magnesium chloride, ammonium zinc chloride, ammonium magnesium phosphate, &c., even after prolonged boiling. Ammonia is completely liberated from these compounds by boiling with sodium hydroxide solution, although a longer time is required than with ammonium chloride. In the cold, the action of soda is very slow, and is not complete until after many days. Sodium hydroxide mixed with magnesia acts almost like the hydroxide alone, but if the substance is first

treated with magnesia and afterwards with sodium hydroxide, the latter is unable to complete the decomposition, even after somewhat prolonged ebullition. These results are due to the formation of double compounds, such as ammonium magnesium oxide, double chlorides, &c. It is evident that in consequence of the limited action of magnesia on ammonium magnesium phosphate and similar compounds, this base cannot be used for the estimation of ammonia in soils and other organic products containing insoluble double ammonium salts. This applies equally to certain derivatives of the aldehydes, and probably also to the ammonium salts of humic acid and its allies. The limited action of magnesia, even on simple ammonium salts, is due to the formation of basic double salts, which are dissociated in presence of water. The authors do not approve of Schloesing's plan of making the substance slightly acid with nitric acid, or dissolving the insoluble phosphates in hydrochloric acid, before estimating the ammonia. C. H. B.

Estimation of Ammonia. By T. Schloesing (*Compt. rend.*, **103**, 227—230, and 301—303).—The author has made further experiments, and finds that ammonia is completely expelled from dilute solutions (0·046 gram NH_3 per litre) by boiling with magnesia or calcium carbonate for 40 minutes, the bulk of the original liquid being about 500 c.c. in each experiment. A large excess of magnesium chloride retards the evolution of ammonia, and necessitates longer boiling, but does not affect the accuracy of the result. Calcium chloride has the same effect, but to a much smaller extent.

Magnesia does not displace the whole of the ammonia from solid ammonium magnesium phosphate, but if the phosphate is dissolved in dilute acid, and the excess of magnesia added to the solution, the ammonia is completely expelled after boiling for about 50 minutes.

It is important to remember that carbonic anhydride is not retained by magnesia, but condenses with the ammonia in the standard acid. It is therefore necessary to boil the acid for a short time before titrating with standard alkali; there is no loss of ammonia if the acid is in excess.

Magnesium ammonium, zinc ammonium, and copper ammonium sulphates, and zinc ammonium and magnesium ammonium chlorides, are completely decomposed by magnesia, with liberation of ammonia. In the author's experiments, a quantity of double salt, corresponding with 0·047—0·083 gram of ammonia, was dissolved in about 500 c.c. of water, 2 grams of magnesia added, and the boiling continued for 45 minutes. C. H. B.

Estimation of Lime in Animal Charcoal by Bolley's Method. By P. Guyot (*J. Pharm.* [5], **13**, 183—185).—In fresh animal charcoal, and especially in that which has been repeatedly employed in sugar refining, the amount of caustic lime may be considerable. The method of estimating this lime, as given by Bolley, is to boil with a solution of ammonium chloride and determine the amount of ammonia set free. Dulong has long ago shown that most carbonates react on ammonium salts at the temperature of boiling water with production

of ammonium carbonate which passes over with the steam. The author shows that this reaction takes place in testing animal charcoal, so that Bolley's method is quite untrustworthy. J. T.

Use of Soap Solution. By G. E. R. Ellis (*Chem. News.*, **54**, 99).—A table is given of results which show that the method for determining the hardness of waters, as frequently worked, is very liable to lead to error, and it is better, and in fact safest, to add the soap solution 1 c.c. or less at a time, and shake well after each addition. D. A. L.

Determination of Ferric Oxide in Presence of Alumina. By E. Donath and R. Jeller (*Zeit. anal. Chem.*, **25**, 361—363).—Ferric oxide, ignited for five to eight minutes in a covered porcelain crucible, with zinc-dust or fine filings, is reduced to metallic iron, which readily dissolves in dilute sulphuric acid, yielding at once a solution fit for titration with permanganate. The solution takes place so rapidly that no precautions to exclude air are needed. Both forms of zinc are liable to contain iron. From the filings, this may be removed by a magnet, but since the action of zinc-dust is more energetic, it is better to use this and correct for the iron it contains. Some samples are, however, unsuitable, owing to the presence of tin. The same process can be applied to iron ores or slags, but those containing ferrous compounds must first be peroxidised by roasting with ammonium nitrate, as otherwise low results are likely to be obtained. M. J. S.

Discrimination of Thin Metallic Films. By L. Loviton (*J. Pharm.* [5], **13**, 227—229).—The author has investigated methods for distinguishing between metallic goods plated with silver, nickel, or tin, and has devised several simple and effective methods. The first consists in heating cautiously a small surface in a Bunsen flame, and noting the colours produced. A white nickel surface gives (1) yellowish-grey coloration; (2) violet reflections; (3) blue coloration with black reflections: (4) finally a uniform grey tint with green reflections. A white tin surface gives (1) dull yellowish-grey coloration; (2) slight violet reflections, rapidly disappearing; (3) grey tint with dotted surface; (4) roughened surface with decidedly yellow spots. A white silver surface gives (1) no change perceptible to the naked eye; (2) white with minute violet dots; (3) passes abruptly to uniform grey with white dots; (4) yellowish-grey rough surface. A single comparative test is sufficient to decide the nature of the surface under examination. On submitting the surfaces to the action of sodium chloride, the second method, the following results are obtained :—Nickel gives a reddish-violet coloration after about 10 minutes. Tin gives a scarcely perceptible dull grey coloration. Silver is unchanged. Similar results are obtained instantaneously on plunging the objects into hydrogen peroxide and adding powdered manganese dioxide. A final method, giving extremely definite results, consists in plunging the objects into dilute ammonium sulphide solution, gently warmed. The silver coating blackens; the tin is dissolved, exposing the surface plated, the nickel remains unchanged. J. T.

Examination of Nickel. By E. Langbein (*Dingl. polyt. J.*, **261**, 495).—Cast or rolled anodes of nickel are frequently contaminated with manganese to such an extent that in determining the metal by electrolysis, part of the manganese is deposited on the cathode, together with the nickel. The following method is said to overcome this difficulty: 2 grams of the nickel are dissolved in dilute nitric acid. The solution is filtered through a tared filter to remove silica and carbon, and the filtrate subjected to electrolysis, having previously added a small amount of sulphuric acid. The copper precipitate is collected, washed, dried, and weighed. The solution is treated with 5 c.c. of sulphuric acid, and evaporated to expel the nitric acid. It is then diluted with 100 c.c. of water, precipitated with ammonia, allowed to remain in a warm place for five or six hours, filtered and washed. The precipitate containing iron and manganese is redissolved in dilute sulphuric acid and reprecipitated with ammonia. After repeating this treatment a third time, the filtrates and washings are made up to 500 c.c. The nickel is then determined by electrolysing 50 or 100 c.c. of this solution, having previously added a corresponding quantity of ammonium chloride and ammonia.

D. B.

Separation of Nickel from Cobalt. By P. Gucci (*Gazzetta*, **16**, 207—209).—In order to detect nickel in the presence of cobalt, the following method is suggested: the mixed sulphides, obtained in the ordinary course of qualitative analysis, are converted into oxides by fusion with potassium nitrate. The fused mass is treated frequently with water, nitric acid of sp. gr. 1·2 is added to the undissolved oxides, and the mixture is heated for about a minute on the water-bath; the nickel oxide is completely dissolved, whilst the cobalt oxide remains unaltered. On filtration, the presence of the nickel is ascertained by precipitation with alkali.

A comparative experiment, with two equal quantities of nickel and cobalt oxides, showed that the former was entirely dissolved before a trace of the latter could be detected in solution. V. H. V.

Separation of Antimony and Tin. By A. Carnot (*Compt. rend.*, **103**, 258—261).—When oxalic acid is added to a feebly acid solution of antimony or tin, a white precipitate of the oxalate is produced, but in presence of ammonium salts much more soluble double oxalates are formed, which only crystallise from highly concentrated solutions and can be mixed with large quantities of water without any precipitation taking place. In this way, perfectly clear, feebly acid solutions of tin and antimony can be obtained. From such solutions hydrogen sulphide precipitates orange antimony sulphide and black stannous sulphide. Stannic compounds are not completely precipitated especially from hot solutions containing a large excess of free oxalic acid. It seems that the true colour of stannous sulphide is black, the ordinary brown colour being due to admixture with some stannic sulphide.

In an oxalic acid solution of a tin compound, sodium thiosulphate produces a white precipitate of sulphur only, all the tin remaining in solution, whilst if a solution of antimony containing either hydro-

chloric or oxalic acid is boiled with sodium thiosulphate, a yellow precipitate is formed which becomes orange and then red and consists of antimony sulphide and oxysulphide. Precipitation is not complete unless the liquid contains some free hydrochloric acid and is heated actually to boiling. If the precipitate is dried at 110°, and then treated with carbon bisulphide to remove sulphur it has the composition Sb_2OS_2.

In order to separate tin and antimony, the hydrochloric acid solution of the two metals is mixed with ammonia or ammonium chloride, about 2 grams of oxalic acid added, the liquid almost neutralised with ammonia, and diluted to 250 to 300 c.c. A solution of sodium thiosulphate is then added in the proportion of 10 parts of the crystallised salt to 1 part of antimony, then 1 to 2 c.c. of dilute hydrochloric acid, and the liquid is boiled for some minutes; the precipitate is allowed to settle and the clear liquid mixed with a few drops of hydrochloric acid. If the liquid remains quite clear, more thiosulphate must be added; if it becomes milky, precipitation is complete; if it acquires a yellow or reddish colour, some antimony remains in solution and more acid and thiosulphate must be added until precipitation is complete.

The antimony precipitate can be weighed as oxysulphide (*vide supra*); or converted into sulphide by heating with the simultaneously precipitated sulphur in a current of carbonic anhydride; or it may be dissolved in hydrochloric acid and estimated volumetrically.

The warm filtrate is saturated with ammonia, the precipitate dissolved in ammonium hydrosulphide, and the solution decomposed with acetic acid. Hydrochloric acid should not be used for this purpose, since it might liberate some oxalic acid which would prevent complete precipitation of the tin. The stannic sulphide is converted into stannic oxide in the usual way. C. H. B.

Separation of Arsenic, Antimony, and Tin. By A. Carnot (*Compt. rend.*, **103**, 343—345).—When sodium thiosulphate is added to a hydrochloric or oxalic acid solution of an arsenious or arsenic compound, a white precipitate of sulphur is first produced and then a yellow precipitate of arsenious sulphide, but if sulphurous acid or an alkaline hydrogen sulphite is previously added to the liquid, the precipitation of arsenic is completely prevented whilst that of antimony is retarded, but is not otherwise affected.

In order to separate antimony and arsenic by means of this reaction, the liquid is mixed with ammonium oxalate, sodium thiosulphate added in proportion to the quantity of antimony present (see preceding Abstract), then sulphurous acid or an alkaline bisulphite and the liquid is boiled for some minutes. If the clear solution gives only a white precipitate on addition of hydrochloric acid or sodium thiosulphate, the precipitation of the antimony is complete. The liquid is filtered, the filtrate heated with excess of hydrochloric acid until all sulphurous anhydride is expelled, and the arsenic precipitated by means of hydrogen sulphide.

If arsenic, antimony, and tin are all present, the antimony is precipitated by the method just described, the filtrate is boiled with a

considerable excess of hydrochloric acid, and hydrogen sulphide is passed into the almost boiling liquid. The arsenic is rapidly precipitated, and if the acid liquid is heated until all excess of hydrogen sulphide is expelled, all the tin remains in solution. The precipitated arsenious sulphide may, however, be treated with hydrochloric acid in order to remove any traces of tin. C. H. B.

Quantitative Estimation of Methoxyl. By S. Zeisel (*Monatsh. Chem.*, **7**, 406—409).—In this paper a description is given of a modification of the author's method for the estimation of methoxyl (this vol., p. 493) in substances not readily volatilised; it consists in the preliminary decomposition of the substance to be analysed by hydriodic acid in a sealed tube. After the reaction is complete, the tube is introduced into an apparatus similar to that previously described, and its finely drawn out end is broken off by means of a mechanical arrangement; the analysis is then conducted as before. Results quoted for methyl alcohol and methyl dichlorobutyrate are satisfactory. V. H. V.

Examination of Ether. By G. Vulpius (*Dingl. polyt. J.*, **261**, 96).—Contrary to the assumption that ether having a sp. gr. of 0·725 to 0·735 is free from heavy oil of wine, the author states that on evaporating a sample of ether having a sp. gr. of 0·722, over 1 per cent. of residue was obtained which consisted essentially of heavy oil of wine and contained only traces of acetic acid and water. D. B.

Estimation of Ethyl Hydrogen Sulphate in Rabel Water. By Gautrand (*J. Pharm.* [5], **13**, 225—227).—Rabel water is obtained by mixing 3 parts of alcohol at 90° with 1 part of sulphuric acid of specific gravity 1·842; the mixture is coloured with wild poppy flowers. There are formed in the mixture ethyl hydrogen sulphate, with traces of common ether and of normal ethyl sulphate. The author sought a method of estimation by converting the ethyl hydrogen sulphate into sulphuric acid and obtained the best results by heating a known weight of the water with an equal weight of potassium nitrate and about double the weight of water. The mixture is evaporated to dryness and fused, dissolved in a little water, and the acid weighed as barium sulphate. In another portion of Rabel water, the free sulphuric acid is titrated with standard baryta water. The difference of the two results gives half the amount of sulphuric acid transformed into ethyl hydrogen sulphate. A particular sample employed gave 23·4 per cent. of sulphuric acid as deduced from the barium sulphate, and 19·74 per cent. by titration, showing that 9·41 per cent. of ethyl hydrogen sulphate was contained in the water. J. T.

Estimation of Fusel Oil in Spirits. By Uffelmann (*Dingl. polyt. J.*, **261**, 439—443).—In order to examine spirits for fusel oil, it is essential to extract the latter with pure ether or chloroform. The mixture is then diluted with water, the ethereal layer separated, and the ether allowed to evaporate by exposure to the air. If fusel oil remains *per se*, its presence is indicated by the odour of the residue.

On adding pure diamidobenzene to the residue and keeping the mixture in a dark place, it rapidly assumes a yellow colour, a reaction which is occasioned by the presence of furfuraldehyde in the fusel oil. On treating the residue with a freshly prepared solution of methyl-violet coloured green by the addition of hydrochloric acid, the original colour of the violet is immediately restored if fusel oil is present in the residue. This reaction is said to be very delicate, and has been employed by the author for approximately determining the quantity of fusel oil in brandy. Bromine gives a yellow colour with fusel oil and pure amyl alcohol. By treating one drop of pure amyl alcohol with 1 c.c. of concentrated sulphuric acid at 60—70°, the mixture assumes a yellow colour, which changes to golden-yellow, yellowish-red, red, reddish-brown, and dark-brown, as the temperature is increased. These solutions exhibit characteristic absorption spectra which are, however, marred by the presence of ethereal oils. It is a remarkable coincidence that fusel oil from potatoes contains more furfuraldehyde than fusel obtained from grain.

Stutzer and Reitmair have modified Röse's method in the following manner:—200 c.c. of brandy is treated with a few drops of potassium hydroxide; four-fifths is distilled off and the volume of the distillate made up to 200 c.c. 50 c.c. is placed in a 100 c.c. flask, sufficient water is then added from a burette to make a 30 per cent. solution of alcohol, after which the flask is filled to the mark with 30 per cent. alcohol. 20 c.c. of chloroform is placed in the carefully dried apparatus, and then the 100 c.c. of diluted distillate and 1 c.c. of sulphuric acid of sp. gr. 1·286. The mixture is well shaken, cooled, and allowed to settle. The apparatus is inclined so that the chloroform runs into the bulb and back again into the tube. After a few minutes the volume of the chloroform is read off, and the amount of amyl alcohol calculated from the subjoined table:—I. Volume increase of chloroform. II. Percentage volume of amyl alcohol:—

I.	0·20	0·35	0·50	0·65	0·80	0·95	1·10	1·25	1·40	1·55
II.	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0

D. B.

Estimation of Glycerol in Wine. By R. Bensemann (*Dingl. polyt. J.*, **261**, 404).—In order to determine the extract containing glycerol, 10 c.c. of wine is evaporated in a flask on the water-bath to a syrupy condition and dried at 95—100° until a constant weight is obtained. The extract free from glycerol is estimated by evaporating 10 c.c. of wine in a small porcelain basin to a stiff syrupy consistence, drying at 110°, and weighing until a constant result is obtained. The glycerol is determined by mixing 100 c.c. of wine with 5 grams of calcium hydroxide in a porcelain dish and evaporating the mixture nearly to dryness on the water-bath. The residue is then mixed with from 5 to 10 grams of gypsum to form a stiff mass and extracted with 50 c.c. of 90 per cent. alcohol in an extraction apparatus. The alcoholic solution is evaporated to a stiff, syrupy consistence, and the residue dissolved in 90 per cent. alcohol. The solution is brought into a 50 c.c. cylinder, graduated in cubic centimetres, and provided with a glass stopper, treated with 20 c.c. of alcohol (90 per cent.), and

made up to 50 c.c. with ether. After settling, 25 c.c. of the solution (corresponding with 50 c.c. of wine) is evaporated to dryness in a flask, dried at 90°, and weighed. The weight, less the ash, represents the amount of glycerol in the wine. D. B.

Estimation of Phenol as Tribromophenol. By H. Beckurts (*Arch. Pharm.* [3], **24**, 561—572).—The author describes the various methods proposed for the estimation of phenol, all based on the formation of insoluble tribromophenol by the reaction of an aqueous solution of phenol with bromine-water. In numerous experiments made with equal amounts of phenol and bromine-water, the results obtained were variable; and this variation the author finds to be due not alone to possible vaporisation of bromine, but also to the formation of tribromophenol bromide. R. Benedict (Abstr., 1885, 1266) has already described the formation of this compound by the action of saturated bromine-water in excess on aqueous phenol solution. The author sought to ascertain why in Seubert's process (Abstr., 1882, 106) more of the bromide was not formed during the process of estimating phenol, and concludes from his investigation that the presence of acid prevents the formation of tribromophenol bromide to any great extent, although not entirely. J. T.

Estimation of Phenol in "Liquid Carbolic Acid." By H. Beckurts (*Arch. Pharm.* [3], **24**, 580—588).—Satisfactory results are obtained, when the article is free from homologues of phenol, by Koppeschaar's method (Abstr., 1883, 124), and also by the empirical methods of Schlickum, Vulpius, and Salzer.

Schlickum's process depends on the increase in volume of the phenol when shaken up with an equal volume of water. A table is given showing the increase corresponding with different percentages of phenol. The method, although exact, has the disadvantage of requiring the measurement of minute volumes, thus a difference of 1 c.c. when 10 c.c. of the phenol is taken, will indicate a difference of 8—10 per cent. of phenol.

Vulpius makes use of the turbidity produced in carbon bisulphide by phenol containing water. The aqueous phenol is run from a burette into, say, 10 c.c. of carbon bisulphide at a temperature of 20° until the turbidity at first produced just disappears on shaking. The more water there is present with the phenol the more solution is required to remove the turbidity. A numerical table is given showing the amount of phenol contained for any given volume run from the burette. Excellent results are given if the temperature be kept exactly at 20°.

Salzer has carried out a method proposed by Vulpius and based on the fact that aqueous phenol will take up the more water without becoming turbid the less water it contained originally. Water is run from a burette into a weighed quantity of the aqueous phenol until persistent turbidity is produced, and the amount of phenol is given by a numerical table. J. T.

Detection of Traces of Hydrocyanic Acid. By G. Vortmann (*Monatsh. Chem.*, **7**, 416—417).—A method for the detection of traces of hydrocyanic acid based on the formation of the nitroprussides by the action of sodium nitrite on potassium cyanide in presence of a ferrous salt. The liquid to be examined is mixed with a few drops of potassium nitrite, three drops of ferric chloride, and so much dilute sulphuric acid as will suffice to dissolve the yellowish-brown basic ferrous salt at first formed to a yellow solution. The mixture is heated to boiling, cooled, the excess of iron removed by a few drops of ammonia, filtered, and the filtrate tested with a few drops of very dilute colourless ammonium sulphide solution. The formation of a violet coloration turning successively blue, green, and violet, indicates the presence of a cyanide. One part of hydrocyanic acid in 312,500 parts water can thus be detected; the reaction therefore is more delicate than the Prussian blue, but less delicate than the thiocyanate reaction. V. H. V.

Determination of Tartaric Acid in Wine Lees and Tartar. By A. Bornträger (*Zeit. anal. Chem.*, **25**, 327—359).—The author has submitted every detail of the methods of Warington (this Journal, 1875, 973) and of Grosjean (Trans., 1879, 341) to an exhaustive experimental investigation.

1. *Solubility of Hydrogen Potassium Tartrate.*—Pure water at 29° dissolves 0·8536 per cent.; at 12·5°, 0·4098 per cent. A 10 per cent. solution of potassium chloride at 29° dissolves 0·0583 gram; at 12·5°, 0·0376 gram in 100 c.c. (Grosjean at 12° found 0·0227). The solubility in potassium chloride is therefore not only much lower but varies less with varying temperature. Both in potassium citrate and in citric acid solutions, it is more soluble than in water, but in a mixture of the two it is less soluble than in water. In a dilute solution (2·7 per cent.) of potassium oxalate, it is less soluble than in water, but on increasing the strength of the oxalate solution the solubility rises, so that with 9 per cent. it is greater than in water. A mixture of citric acid and potassium oxalate dissolves less than either separately, but here also the solubility rises with increase in the strength of the oxalate solution.

2. *Warington's Process.*—The quantity of material prescribed by Warington (2—2·5 grams of tartaric acid) is not sufficiently precise. For 2·5 grams of tartaric acid 2 grams of citric acid is insufficient; 2·5 grams of citric acid gave better results, but the percentage obtained varied with the amount of tartaric acid present, and this variation became still greater when 3 grams of citric acid were used. The best result (99·02 per cent.) was obtained by using 3 grams of citric acid when 3·5 grams of hydrogen potassium tartrate (2·7926 of tartaric acid) were present, but working in the same way only 97·76 per cent. was obtained from 2·5 grams of tartrate (1·9947 grams of tartaric acid). The preliminary approximate determination cannot be dispensed with.

3. *Grosjean's Method.*—The addition of 5 grams of potassium chloride (to 50 c.c.) at once raises the results 2—2·5 per cent, and reduces the effect of variations of temperature (10°) to an insignificant

amount (0·2 per cent.). Although, in the absence of potassium citrate and citric acid, oxalate greatly increases the solubility of the tartrate in potassium chloride, yet when precipitating with citric acid from a neutral solution of the tartrate in 10 per cent. potassium chloride, the presence of 1·5 to 3·0 grams of oxalate is beneficial, raising the yield to 99·5 per cent. of the tartaric acid employed. A larger quantity of oxalate again depresses it. But the greatest advantage of the presence of potassium chloride is that, when the quantity of citric acid used is increased to 3 grams, widely varying amounts of tartrate (1·5 to 4·0 grams) can be employed with practically identical percentage results (99·3 to 99·7 per cent.) The preliminary approximate determination therefore becomes unnecessary, since by using 7·5 grams of lees, or 3·75 grams of tartar, the amount of tartrate present will in almost all cases fall within the above limits. Using these quantities, the number of cubic centimetres of normal alkali required by the precipitate gives at once (when multiplied by 2 for 7·5 grams, or by 4 for 3·75 grams) the percentage of tartaric acid present. For washing, it is better to use Klein's 10 per cent. solution of potassium chloride saturated with acid tartrate than Grosjean's 5 per cent. solution, and it is convenient after heating with oxalate (for half an hour) to dilute with 100 c.c. of hot water before neutralising, and to concentrate to 50 c.c. after filtering, M. J. S.

Drying Fats. By A. Sonnenschein (*Zeit. anal. Chem.*, **25**, 372—373).—Fats cannot be dried by simply heating at 100—110°, since the water subsides to the bottom. By aspirating dry air through the fat while it is heated on the water-bath, however, the moisture can be completely removed. M. J. S.

Examination of Fats and Oils. By E. Dieterich (*Zeit. anal. Chem.*, **25**, 431—432).—The author, after numerous experiments on the sp. gr. of oils, and on the saponification, elaïdin, nitric acid, and sulphuric acid tests, and Bach's process (*ibid.*, **23**, 259), concludes that even those tests which distinguish pure oils fail with mixtures. The elaïdin and nitric acid tests are comparatively speaking the best. M. J. S.

Presence in Filter-paper of Matter soluble in Ether. By P. Vieth (*Landw. Versuchs-Stat.*, 1886, 203—206).—Adams in 1885 recommended that the estimation of the fat in milk should be effected by extracting the fat with ether from filter-paper which had previously been soaked in the milk and then dried. The author shows that ether extracts from the paper other substances, having an aromatic vanilla-like odour. The amount of extract is but small, affecting the results by only 0·03 per cent., or at the most under unfavourable circumstances by 0·06 per cent., but seeing that by means of centrifugals only about 0·2 per cent. of fat is left in the skim milk, this 0·03 per cent. is no longer unimportant. E. W. P.

Quantitative Estimation of Chlorophyll. By A. Hansen (*Bied. Centr.*, 1886, 476).—The leaves are boiled for some time, the colouring matter extracted by 96 per cent. alcohol, the solution saponi-

fied, and after evaporation of the solvents, dried and weighed. The average quantity found in various leaves was 5·142 grams per 1 sq. metre. Employing Sach's calculations, it appears that in the gourd leaves 25 grams starch are produced through the agency of 5 grams of chlorophyll. The author considers that these figures point to the conclusion that the whole of the chlorophyll present is not employed in producing starch. E. W. P.

Reaction for Distinguishing the Natural Colouring Matters of Wine from Added Coal-tar Colours. By C. Blarez and G. Denigés (*Bull. Soc. Chim.*, **46**, 148—151).—10 c.c. of the wine is treated with 10 drops of glacial acetic acid, heated to 100°, and 0·2 gram of powdered mercuric acetate added, the mixture shaken rapidly, cooled and filtered; any coal-tar colouring matters then pass through into the filtrate, whilst all the natural wine colouring matters remain on the filter as a lake; when only a mere trace of the artificial colouring matter is present, it may not be readily seen in the filtrate and may be partly held by the precipitate. In this case, the precipitate is drained, and then washed by pouring 5 or 6 c.c. of alcohol, containing some drops of acetic acid, through the filter several times, by which means any coal-tar colours are extracted; the artificial colouring matters in the solutions may then be examined, the reactions of about 20 being described in the paper. A. P.

Investigation of Tannin Extracts. By F. Simand and B. Weiss (*Dingl. polyt. J.*, **260**, 564—568).—For the estimation of tannin, hide powder is essentially employed by the authors. Raw skin is washed, depilated, treated with dilute hydrochloric acid, and dried in a stretched position; it is then planed into thin shavings, dried, ground, and sifted; the aqueous extract from 5 grams of this powder yields only 36 mgrms. of solid matter containing 8 mgrms. of ash.

The estimation of the water and ash is effected by evaporating to dryness from 2 to 3 grams of the tannin extract in a platinum dish on a water-bath, weighing and carefully igniting the residue. The total soluble matter is determined by dissolving 22—28 grams in the case of liquid extracts, and 12—16 grams in the case of solid extracts, in hot water, cooling, making up to 1 litre, and filtering. 100 c.c. of the clear filtrate is then evaporated in a platinum dish on a water-bath, dried, and weighed. The weight, after deducting the ash, gives the total amount of organic matter soluble in water. It is not advisable to determine the amount of insoluble matter directly, owing to the difficulty experienced in filtering and washing the aqueous extract. To estimate the non-tannin matter, 250 c.c. of the clear tanning solution is transferred to a dry Erlenmeyer flask, treated with 1 gram of hide powder, agitated for several hours, and filtered through cotton. This operation is repeated twice, and the third filtrate treated with 2 grams of hide powder. In most cases, this quantity (5 grams) is sufficient to completely remove the tannin materials. The solution is then filtered clear through paper. 100 c.c. of the filtrate are evaporated and dried. The weight, after deducting the ash, gives the amount of non-tannin matter. This process is said to give more accurate results than

Löwenthal's method, as a difference of 8 mgrms. corresponds with 0·29 per cent. of tannin only, a quantity which is indicated by 0·1 c.c. of permanganate solution.

A number of extracts were analysed by the authors, the results being embodied in a table giving the percentages of total tannin, non-tannin matter, water, ash, and insoluble matter, also the amount of tannin estimated according to Löwenthal's method.

It is shown that bark extracts contain more ash than wood extracts, hence the determination of the ash may form a mark of distinction between bark and wood extracts, especially as the ash of the former gives a distinct reaction for manganese, whilst the ash of wood extracts contains only traces of this substance. By shaking a concentrated aqueous solution of quebracho extract with ethyl acetate, the ethereal layer assumes a dark-green colour. Sumach extracts are characterised by the high percentage of ash constituents and the peculiar odour resembling tea. D. B.

Separation of Urethane. By G. Jacquemin (*Compt. rend.*, **103**, 205—207).—If a solution of urethane is mixed with mercuric chloride and then with potassium hydroxide, a bulky, white precipitate is formed, which dissolves when heated in presence of excess of urethane, but separates again on cooling. The precipitate is insoluble in and unaffected by alcohol and ether, but in presence of excess of potash it becomes yellow owing to the formation of mercuric oxide. If the urethane is first mixed with potash and then with mercuric chloride, the precipitate is at first yellow but becomes white on shaking. Freshly precipitated mercuric oxide dissolves when heated with urethane, and a white precipitate separates on cooling, but if the action of heat is prolonged, a black substance separates and floats at the surface of the liquid. Urethane is distinctly precipitated by mercuric salts in solutions containing 0·15 per cent. If a solution containing only 0·05 gram of urethane per litre is mixed with potash and mercuric chloride added drop by drop, the yellow precipitate which forms redissolves so long as any urethane remains unaltered, and then becomes permanent. This reaction may be employed for the volumetric estimation of urethane; 0·1 gram of which in 10 c.c. of water, mixed with excess of potash, requires 10 c.c. of a solution of 30·44 grams of mercuric chloride per litre to produce a permanent precipitate.

Mercuric nitrate and acetate also precipitate urethane, but only in presence of potash, whereas they precipitate urea from a simple aqueous solution. These reagents serve to separate urea from urethane. Mercurous nitrate produces a black precipitate. Silver nitrate alone gives no reaction, but on subsequent addition of potash, a brick-red precipitate is formed which rapidly turns black.

To detect urethane in urine the latter is repeatedly shaken with ether, the ether being afterwards washed with water. The ethereal solution is evaporated, and the residue dissolved in water and treated as above, the quantity being estimated volumetrically if necessary.

Urethane decomposes slowly in presence of alkalis in the cold, and much more rapidly at 30°. C. H. B.

Comparative Experiments on the Methods of Determination of Morphine in Opium. By V. Venturini (*Gazzetta*, **16**, 239—246).—In this paper, the various gravimetric and volumetric methods proposed for the determination of the proportion of morphine in opium are compared. As a result of the examination it would appear that most of the methods are unsatisfactory as giving either too low results or yielding impure morphine. Of the gravimetric methods, the preference is given to those of Flückiger (Abstr., 1885, 1165) and of Conroy, which is adopted by the American pharmacopeia; of the volumetric methods, the simplest and most exact is Kieffer's, which consists in the reduction of a solution of potassium ferricyanide standardised by a solution of sodium thiosulphate. V. H. V.

Optical Method of Analysis of Quinine Sulphate. By D. Hooper (*Pharm. J. Trans.* [3], **17**, 61—62).—The results of experimental analyses of different samples of quinine sulphate have convinced the author of the accuracy of the optical method of analysis (compare this vol., p. 813). The tartrates are the best salts for the purpose, inasmuch as the proportion of combined water in them is more constant than in the other salts. Samples of quinine sulphate were examined both before and after recrystallisation; in all cases, the numbers for the percentage of quinine and cinchonidine obtained in the first instance by observation and calculation were confirmed in the second, where the recrystallised salt and the mother-liquor were examined separately and the results added together. The author has observed a relation between the amounts of the lævorotatory alkaloïds in distinct species of cinchona: for example, in *C. officinalis* bark the quantity of quinine is twice that of the cinchonidine, whilst in *C. succirubra* bark the quantity of cinchonidine is double that of the quinine. It is noted that a very few recrystallisations are sufficient to obtain quinine sulphate quite pure.

D. A. L.

Estimation of Emetine. By H. W. Jones (*Pharm. J. Trans.* [3], **17**, 277—279).—A mode of working the lime method successfully is described, and recommended for the estimation of emetine in ipecacuanha wine, &c., whilst Flückiger's method of extracting the drug with chloroform and a small quantity of ammonia is acknowledged to be superior for such estimations as in ipecacuanha, inasmuch as it is less troublesome and extracts all the alkaloïd in an unaltered condition. In working the volumetric method with Mayer's solution, it is important to remove all extraneous matter and to work uniformly; dilution makes a great difference, and a table of factors is given for correcting for the latter defect. Ipecacuanha rarely contains more than 1·0 per cent. of emetine. Experimental evidence is adduced to show that although a change takes place during the working of the lime method, the full weight of emetine is obtained, because the altered emetine is extracted with the unaltered alkaloïd. With regard to the action of heat: on a water-bath the alkaloïd at first lost water, then remained constant in weight during two hours, after which period it regularly increased in weight. The emetine recovered, either after lime treatment or heating, yielded coloured acid solutions, from which

chloroform extracted some substance, amounting in the case of lime to 16·8 per cent. of the whole, and in cases of heating on the water-bath for 10 hours, to 12·25 per cent., and for 14 hours, to 13·25 per cent. In acetic solutions of emetine, a similar alteration takes place.

D. A. L.

Estimation of Cocaïne by Mayer's Reagent. By A. B. Lyons (*Pharm. J. Trans.* [3], **16**, 1094—1095).—In solutions of cocaïne, Mayer's reagent produces a precipitate of variable constitution which cannot be washed with water without loss; moreover, an excess of the reagent, amounting to about 8·5 per cent. of the solution, is required for complete precipitation. This reagent cannot, therefore, be used for making accurate quantitative estimations of the alkaloïd; and trustworthy approximate estimations can only be obtained by working under similar conditions. When titration is resorted to, the solutions should contain about 1 of alkaloïd in 400, and a correction must be made for the above excess. Full directions for working are given in the paper. The addition of potassium iodide to the solution, or the use of a modified Mayer's reagent containing five instead of three equivalents of potassium iodide, improves the process to a certain extent. When examining coca-leaves, about 2 per cent. more alkaloïd is indicated by Mayer's reagent than can be obtained by extraction with ether and chloroform. D. A. L.

Quantitative Separation of Albumin from Peptones. By H. Weiske (*Landw. Versuchs-Stat.*, **33**, 147—152).—The author refers to Szymanski's experiments (Abstr., 1885, 822) which seem to prove that peptones are not precipitated from neutral aqueous solutions by copper hydroxide, and that they can be separated from albumin by this reagent; this assertion is not borne out by facts, moreover, the use of metallic hydroxides for the precipitation of albumin is not new. Hoffmeister has described a process, but he concludes his description with the remark, "the greater portion of the peptones pass into the filtrate," indicating that some remained in the precipitate; the author has carefully investigated the subject, and finds that the albuminous precipitate always contains peptones, and when large quantities are operated on, the error introduced into analyses may be considerable if this is overlooked. Dogiel in his work on milk takes the same view, and Stutzer admits the fact, so that it may be taken as proved that the figures will always be too high when albumin is estimated by metallic oxides in presence of peptones. J. F.

Distinction between Albuminoïds, Gelatin, and Peptones by the Capillarimetric Method. By G. Bodländer and J. Traube (*Ber.*, **19**, 1871—1876).—The presence of albumins or gelatin in solution has but little effect on the height at which water stands in a capillary tube; peptones on the other hand cause a considerable diminution of the capillary height. As the tendency of these liquids to coagulate, &c., causes considerable difficulty in the direct measurement of the capillary height, the authors have availed themselves of the fact (proof of which will be given in another paper) that the volume of the drops formed at the lower end of a capillary tube (cut

at right angles to the axis of the tube and with the cut surface placed horizontally) is proportional to the capillary height. The number of drops therefore formed by a given volume of liquid caused to flow through such a tube will be inversely proportional to its capillary height. It is shown that quantitative results may be obtained by this method, and a table is given of determinations made with peptones from various sources in solutions of different strengths.

A. J. G.

Microchemical Detection of Albuminoïds in Seeds. By F. Szymanski (*Landw. Versuchs-Stat.*, 1886, 229—230).—The author employs a method slightly different from that of Piotrowski and others. When seeds of rye and wheat are examined for albuminoïds, they are placed in dilute copper sulphate solution for 12—24 hours, and then, after drying between filter-paper, are cut into the usual microscopic sections. Being placed on the object carrier, they are moistened with dilute soda or potash solution, when, if the section is not too thick, the blue coloration (biuret reaction) is produced. The cellulose structure immediately below the embryo becomes blue-violet, whilst the interior of the embryo assumes a rose-red colour. This is evidence that in the embryo, as well as in the germinated seed, peptone (hemialbumose) is pre-existent. E. W. P.

New Method of Distinguishing Vegetable from Animal Fibre. By H. Molisch (*Dingl. polyt. J.*, **261**, 135—138).—The following process depends on the application of two new reactions for sugar lately discovered by the author (this vol., p. 923):—About 0·01 gram of the sample, previously well boiled and washed with water, is mixed first with 1 c.c. of water, then with 2 drops of an alcoholic solution of α-naphthol (15—20 per cent.), and finally with an equal volume of concentrated sulphuric acid. In the case of vegetable fibre, the solution assumes, immediately after shaking, a deep-violet colour, the fibre being dissolved. If, however, the fibre is of animal origin, the liquid assumes a colour varying from yellow to reddish-brown. By substituting a solution of thymol for α-naphthol, a fine carmine colour is obtained in the place of the violet.

The author has successfully applied this test to different vegetable fibres, such as cotton, hemp, jute, china-grass, &c.; also to the cellular tissues of wood, cork, and fungi. Moreover, in the case of dyed fabrics, the colouring matters present do not appear to interfere with the success of the reaction. D. B.

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ERRATA IN VOL. XLVIII.

Page	Line	
973	16 from bottom,	*for* "parabromobenzene" *read* "parabromotoluene."
1240	16 and 17 from top,	*for* "dihydroxydimethylanthrarufin" *read* "dimethylanthrarufin."

ERRATA IN VOL. L.

Page	Line		
75	9 from top	*for* "acetophenoneacetate" *read* "acetophenoneacetoacetate."	
76	17 „ „		
174	19 „ bottom	*for* "with ammonia" *read* "into ammonia."	
„	18 „ „ „	"with nitric acid" „ "into nitric acid."	
175	17 „ top „	"solution" „ "substance."	
194	7 from bottom „	"Ce" „ "Cl."	
324	4 „ „ „	"melene" „ "melem."	
536	11 and 17 from bottom,	*for* "thienyl" „ "thenyl."	
546	19 and 24 „ top „	"benzylidine" *read* "benzylidene."	
556	5 from bottom	*for* "$(OH)_5=1:2:3:1':3'$" „ "$(OH)_5=1:2:3:2':4'$".	
608	23 „ top „	"dextrose" „ "levulose."	
700	3 „ bottom „	"ferrocyanide" „ "ferricyanide."	
788	4 „ „	after the word "was" *insert* "converted into the sulphonamide and this."	
800	27 „ top	*for* "benzilhydroxamide" *read* "benzil hydrocyanide."	

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